

**SYNTHETIC ASPECTS OF  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)(\text{E}'\text{Ph}_3)\text{X}]$ , THEIR  
REACTIONS WITH N-BASES, TERMINAL ACETYLENES AND  
SYNTHESIS OF CYANOBRIDGED DINUCLEAR SPECIES  
( $\text{E}, \text{E}' = \text{P}, \text{As}, \text{Sb}$ ;  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{H}, \text{CN}, \text{NCS}, \text{SnCl}_3$ )**

A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of

**DOCTOR OF PHILOSOPHY**

by  
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to the

**DEPARTMENT OF CHEMISTRY  
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR**

**MAY, 1987**

**Dedicated**  
**To**  
**My Parents**

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STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor U.C. Agarwala.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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May 11, 1987



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Chm 542 Advanced Inorganic Chemistry II  
Chm 646 Bioinorganic Chemistry  
Chm 800 General Seminar  
Chm 801 Special Seminar  
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CERTIFICATE II

Certified that the work contained in this thesis entitled:  
"Synthetic Aspects of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)(\text{E}'\text{Ph}_3)\text{X}]$ , Their Reactions with N-Bases, Terminal Acetylenes and Synthesis of Cyano-bridged Dinuclear Species ( $\text{E}, \text{E}' = \text{P}, \text{As}, \text{Sb}; \text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{H}, \text{CN}, \text{NCS}, \text{SnCl}_3$ )" has been carried out by Mr. K. Mohan Rao under my supervision and that the same has not been submitted elsewhere for a degree.

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## PREFACE

One of the most interesting and important areas in which temporary inorganic chemists could contribute profitably is organometallic chemistry, a broad interdisciplinary field whose sphere of interest includes all compounds wherein metal usually in low valence state is bonded through carbon of an organic molecule, radical or ion. Since the publications of the synthesis of Zeise Salt (1848), and Victor Grignards' organomagnesium compounds (1900), there have been spasmodic references to the syntheses of such novel compounds as ferrocene, ruthenocene etc. From the middle of the present century and particularly from the syntheses of the cyclopentadienyl transition metal complexes there came a vast blossoming of Organic-Transition Chemistry which has led into the development of a large number of new areas like homogeneous catalysis, etc.

In the organometallic compound  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ , prepared by Wilkinson (1969) and later by a different route by Bruce and Windsor (1977), the pronounced steric action and the presence of high electron density on the metal center resulting from two bulky tertiary phosphine ligands possibly been responsible for its much unusual chemistry. Furthermore, the ready substitution of one of the  $\text{PPh}_3$  molecules by other donor groups and/or the ease of scission of Ru-Cl bond in methanolic solution has engendered an intense interest

in its potential synthetic utility for the preparation of its large number of cationic and neutral substituted derivatives, thus making  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  as one of the most versatile organoruthenium(II) complex of contemporary interest. The work embodying the present thesis is also an attempt in this direction.

The subject matter of the first chapter reflects the scope and the objective of the work dealt in the thesis where we have examined the substitution reactions of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{X}]$  with a large number of other donor molecules like arsine, stibine, acetylenes, etc. It also introduces, though in a concise way, the present status of the ruthenium cyclopentadienyl chemistry emphasizing those aspects which have a bearing on the present work.

Chapter II and III encompasses (i) The synthesis of  $\text{AsPh}_3$  and  $\text{SbPh}_3$  analogues of the complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  as well as mixed ligand complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)(\text{E}'\text{Ph}_3)\text{Cl}]$  ( $\text{E}, \text{E}' = \text{P}, \text{As}, \text{Sb}$ ); (ii) Interconversion of these complexes; (iii) Reactions of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{Cl}]$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ ) with halides like  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , pseudo halides like  $\text{CN}^-$ ,  $\text{NCS}^-$ ,  $\text{SnCl}_3^-$ ,  $\text{H}^-$  along with insertion reactions with  $\text{SnCl}_2$  and (iv) The reactions of these complexes with neutral ligands like MeCN forming cationic complexes. The products have been characterised by microanalytical and various physico-chemical data.

Chapter IV describes the reactions of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ ;  $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-, \text{NCS}^-, \text{SnCl}_3^-$ ) with N-bases

like pyridine,  $\gamma$ -picoline, 2,2'-bipyridine, o-phenanthroline and the reactions of the parent complexes having halide counter anions, with sulfur donor ligands like dithiocarbamate. The interesting aspects of these reactions are the formulation of cationic complexes with 2,2'-bipyridine and o-phenanthroline in which only one of the  $\text{EPh}_3$  ligands has been substituted by a N-base, suggesting the lability of only one  $\text{EPh}_3$  molecule. Tentative structures, have been proposed on the basis of the results of various physico-chemical data.

In Chapter fifth, syntheses of the cyanobridged bimetallic compounds have been described as a result of reactions of cyano complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)\text{CN}]$  ( $\text{E} = \text{P, As, Sb}$ ) with  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{Cl}]$ . Their tentative structures have been proposed on the results of various physico-chemical studies.

Sixth Chapter deals with the reactions of the parent halide complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{Cl}]$  with  $\gamma$ -hydroxy acetylenes. These reactions were divided into two groups. Group (A) deals with reactions of phenylacetylene, propargyl alcohol and ethynyl-cyclohexanol to give cationic  $\eta^1$ -vinyl,  $\eta^1$ -allenylidene and neutral  $\eta^1$ -ethynyl complexes and group (B) deals with the reaction of the substituted propargyl alcohols ( $\text{HC}\equiv\text{C-CMe}_2\text{OR}$ ) ( $\text{R} = \text{Me or Et}$ ) which yielded unexpected dimeric bimetallic cationic complexes.

Tentative structures and mechanism of the formation of these complexes have been postulated on the basis of the results of various physico-chemical studies.

Chapter VII summarizes briefly the results of the work described in the previous chapters and ends with a few proposals for future work.



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## Chapter I

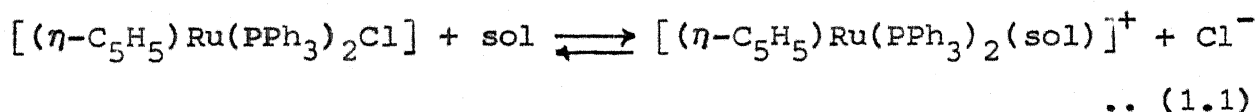
### INTRODUCTION

#### I.1 Scope and Purpose

The ruthenium complex containing cyclopentadienyl and triphenylphosphine as coligands,  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  is one among a few most remarkable molecules which have been recently synthesized (1969).<sup>1</sup> Among its many unusual properties studied by many groups, its rich variety of reactions are rather fascinating. The literature survey reveals the excellent works of Bruce et al.,<sup>2-4</sup> Treichel et al.,<sup>5-7</sup> Selegue et al.,<sup>8-10</sup> Davies et al.,<sup>11,12</sup> Haines et al.,<sup>13</sup> and Wilczewski, et al.,<sup>14,15</sup> who have not only proved unambiguously that the complex is the most attractive molecule for synthetic manipulations, but its reactions have led into other vast and interesting areas of organo-ruthenium compounds. It has been suggested that the enhancement of its chemical reactivity has been a result of relatively high electron density on the metal center and the presence of two bulky  $\text{PPh}_3$  molecules leading to a great steric imposition. Although, an infinitely large number of substitution reactions

could be studied, a knowledge of factors that control these reaction will be of great relevance. Thus, a key question out of many which one would like to answer is, whether these reactions are kinetically and/or thermodynamically controlled? (A few of the similar problems which we plan to tackle are listed in the concluding chapter.)

Among all the substitution reactions carried out until now, one type has been centered around the reactions of Ru-Cl bond resulting in the replacement of chloride either by other anions or by neutral ligands to yield neutral or cationic complexes of the type  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{L})]$  or  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{L})]^+$ . These are possibly based on the following equilibrium<sup>13,16-19</sup> that lies largely to the right in polar solvents like MeOH, DMSO, etc:



Another type has been the substitution of one of the  $\text{PPh}_3$  molecules by various ligands like alkynes, heterocyclic molecules, etc. In addition, a third possibility of reactions, though very little studied, is to activate  $\text{C}_5\text{H}_5^-$  group in order to determine the nature of the aromaticity of the  $\text{C}_5\text{H}_5$  ring in the complex. We believe that there should exist a relationship between the aromatic character of  $\text{C}_5\text{H}_5$  ring and the degree of electron density on the metal center, which, in turn should be a function of the ligands attached to it.

The primary motive of our studies described in the thesis is the synthesis of the arsine, stibine and the mixed ligand analogues of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  either by substitution or by using  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  as the starting material, followed by the reactions of the products thus obtained, with N-heterocyclic bases. These reactions may not only be of some help in understanding the nature of substitution reaction on the metal center, but will also give a clue about the electronic and the steric effects influencing their syntheses.

There has been a considerable activity regarding the reactions of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  with substituted acetylenes.<sup>4,8-10,20-23</sup> The observation that the final products of these reactions sometimes are acetylenic-substituent group dependent, has motivated us to carry out a few reactions in this direction as an extension of the work, using substituted derivatives of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$  as precursors which have been synthesized by us. Such reactions might possibly lead us to the isolation of some novel and exciting acetylenic complexes of ruthenium.

Another facet of our interest in the synthetic reactions of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{CN}]$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ ) is the nucleophilic character of nitrogen end of the cyanide group. Though an initial study has already been made using  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{CN}]$  as the starting material and which yielded cyano bridged<sup>12</sup> ruthenium complexes,

a further study in this direction might help us in bringing out a correlation between the nucleophilicity of nitrogen end of CN group and  $\pi$  and  $\sigma$  character of the coligands attached to ruthenium.

With these aims under consideration we have carried out this project, the various facets of which are:

(a) (i) Attempts to synthesize arsine and stibine complexes of the type  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)\text{Cl}]\cdot\text{CH}_2\text{Cl}_2$  and analogues starting from  $\text{RuCl}_3\cdot x\text{H}_2\text{O}$  and  $\text{AsPh}_3$  or  $\text{SbPh}_3$ ; the reactions of the products with N-heterocyclic bases (Chapter II). (ii) Syntheses of complexes of the type  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)(\text{E}'\text{Ph}_3)\text{X}]$  ( $\text{E} = \text{E}' = \text{P}, \text{As}$ ;  $\text{X} = \text{halogens, and pseudo halogens}$ ) (Chapter II).

(b) Syntheses of complexes of the type  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{X}]$  (Chapter III).

(c) Syntheses of complexes of the type  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)(\text{L-L})]^+\text{Y}^-$ ,  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)\text{LX}]$  ( $\text{L-L} = \text{bipy, o-phen, dtc, acac}$ ;  $\text{L} = \text{Py, } \gamma\text{-pic}$ ;  $\text{Y}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-, \text{NCS}^-, \text{SnCl}_3^-, \text{BPh}_4^-, \text{HgCl}_3^-$ ;  $\text{X} = \text{halides and pseudo halides}$ ) (Chapter IV).

(d) Synthesis of cyano bridged dinuclear cationic complexes  $[(\eta\text{-C}_5\text{H}_5)(\text{EPh}_3)_2\text{Ru-CN-Ru}(\eta\text{-C}_5\text{H}_5)(\text{EPh}_3)_2]^+\text{Y}^-$  (Chapter V).

(e) Reactions of the complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{Cl}]$  ( $\text{E} = \text{P, As, Sb}$ ) with phenylacetylene,  $\gamma$ -hydroxy acetylenes ( $\text{HC}\equiv\text{C-CR}_1\text{R}_2\text{OH}$ ) to form  $\eta'$ -vinylidenes,  $\eta'$ -allenylidenes,  $\eta'$ -alkynyl and dimeric cyclohexene bridged dinuclear complexes (Chapter VI).

Considering the fascinating chemistry of the complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$ , it will be appropriate to have a concise overview of the work carried out so far. The following section is an attempt in this direction.

During the past eighteen years the chemistry of  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{PPh}_3)_2\text{Cl}]$  (I), since its first synthesis in 1969 by Wilkinson et al.<sup>1</sup> has grown so large that one has to make quite arbitrary assumptions regarding the matter to be emphasized in a concise presentation of this nature.

Its versatility as a synthetic precursor because of the variety of substitution reactions it undergoes, which is possibly due to high electron density at the metal center and the lability of one of the phosphine molecules, is responsible for the vast volume of literature available during the last one decade. To account for the novelty of its varied reactivity, one could think in terms of activation of different portions of the molecule under different reaction conditions, viz., the activation of Ru-Cl, Ru- $\eta\text{-C}_5\text{H}_5$ , Ru-L (L =  $\text{PPh}_3$ , etc.) bonds.

## I.2 Reactions at the Metal-Phosphorous Bond

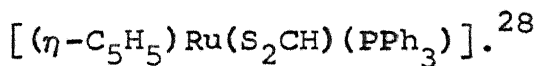
The important factor in the reaction concerning the activation of M- $\text{PPh}_3$  bond of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{X}]$  is the lability of one of the  $\text{PPh}_3$  molecules which can be substituted by a monodentate ligand. In addition, there is also a possibility of

substituting the second molecule of  $\text{PPh}_3$  but the latter reaction usually takes place under stringent experimental conditions. Thus, a stepwise replacement occurs in the reactions with  $\text{PMe}_3$  to give  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cl}]$  at  $80\text{--}100^\circ\text{C}$  and  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{PMe}_3)_2\text{Cl}]$  at  $110^\circ\text{C}$ .<sup>5-7,24,25</sup> In case of dppm or dppe, one or both  $\text{PPh}_3$  molecules can exchange depending upon the reaction conditions.<sup>26,27</sup> The substitution of  $\text{PPh}_3$  by phosphites requires severe conditions. Heating for a short period in decalin yields  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{P}(\text{OR})_3)_2\text{Cl}]$ <sup>26,28</sup> ( $\text{R} = \text{Me}$  or  $\text{Ph}$ ). In the latter case some amount of the cyclometallated derivative has also been formed by the loss of  $\text{HCl}$  as side product.<sup>29</sup> Some of the similar reactions are tabulated in Table I.1.

### 1.3 Reactions at the Metal-X Bond ( $\text{X} = \text{halide ion, CN, NCS, etc.}$ )

#### (a) Metal-Cl Bond

The chloride ion in  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  can be replaced by other anionic ligands (e.g.,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{H}^-$ ,  $\text{CN}^-$ ,  $\text{NCS}^-$ , etc.) to yield thermally stable products  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{X}]$ .<sup>13,14,30,31</sup> Thus, the hydride is obtained by reacting the phosphine complex with  $\text{LiAlH}_4$ .<sup>31</sup> A convenient and facile route to synthesize hydrides,<sup>28</sup>  $[(\eta\text{-C}_6\text{H}_5)\text{Ru}(\text{LL}')\text{H}]$  ( $\text{L}, \text{L}' = \text{PPh}_3$ , dppm, dppe;  $\text{L} = \text{PPh}_3$ ,  $\text{L}' = \text{CO}$ ,  $\text{CNBu}^t$ ) was, however, described by Chatt and Shaw,<sup>32</sup> by using alcoholic base. These hydrides react with  $\text{CHCl}_3$  or  $\text{CCl}_4$  to give chlorides, and with  $\text{CS}_2$ , to form  $\eta'$ -dithioformates, some of which enter into chelation on heating, as in the case of

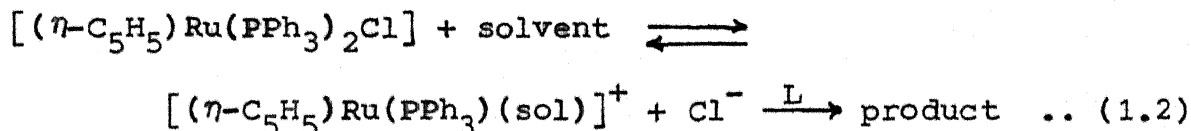


The reaction of  $\text{NaBH}_4$  with the phosphine complex gives a white product<sup>31</sup>  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{H}_2\text{BH}_2)(\text{PPh}_3)_2]$ , and a fluxional molecule  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{B}_3\text{H}_8)(\text{PPh}_3)_2]$ .<sup>31</sup>

Bright yellow complexes of trichlorostannate  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{PR}_3)_2\text{SnCl}_3]$ <sup>6,31</sup> ( $\text{R} = \text{Me}$  or  $\text{Ph}$ ) have been synthesized by the insertion of tin(II) chloride into Ru-Cl bond.

Alkyl complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{R}]$  have been prepared by treating appropriate organolithium reagents with phosphine complex, e.g.,  $\text{R} = \text{Me}$ ,  $\text{C}_6\text{F}_5$ .<sup>31</sup> Though  $\text{PhMgI}$  was used to synthesize a benzoderivative  $\text{MeMgI}$  yielded the iodocomplex.<sup>31</sup>

The formation of all the above complexes occur by facile displacement of the weakly bound solvent molecule from the solvated cation.<sup>13,16-19</sup>



## (b) Synthesis of $\eta'$ -Vinylidenes, $\eta'$ -Propadienylidene, $\eta'$ -Acetylides and Their Reactions

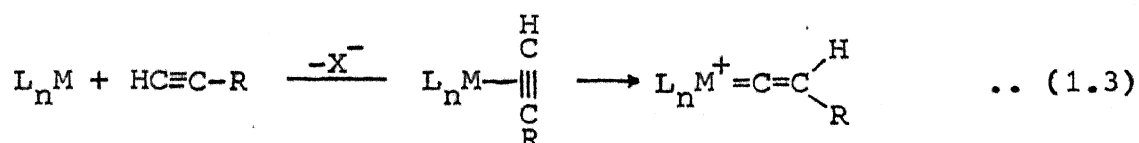
### Synthesis of $\eta'$ -Vinylidenes

Vinylidenes (methylene carbenes)  $(:\text{C}=\text{C} \begin{smallmatrix} \text{R} \\ \diagup \\ \text{R} \end{smallmatrix})$ , which are unstable in the free state, form stable complexes with transition



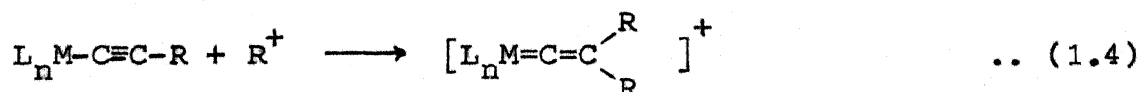
metal ions, similar to carbonyl or isonitrile groups. They may be classified as two electron donors and act as terminal and bridging ligands.<sup>33</sup>

Terminal acetylene (1-alkynes) complexes undergo a 1,2-hydrogen shift to give vinylidene complexes<sup>3,21,23</sup> proceeding via an intermediate,  $\eta^2$ -alkyne complex which in some cases has been isolated or detected spectroscopically;<sup>3,22,34-36</sup>



( $L_nM = Mn(CO)_2(\eta-C_5H_5)$ ,  $Re(CO)_2(\eta-C_5H_5)$ ,  $Fe(dppe)(\eta-C_5H_5)$ ,  $Ru(PPh_3)_2(\eta-C_5H_5)$ ;  $X =$  solvent, halide or CO; the  $C_5H_5$  group may also be substituted by one or two Me groups).

Protonation or alkylation of several ethynyl-metal derivatives gives the corresponding complexes in high yield.<sup>23,37</sup> This is a convenient route for the synthesis of disubstituted vinylidene complexes as well as the parent compounds, which cannot be obtained from 1-alkynes.  $[R_3O]^+$  ( $R = Me, Et$ ) or  $H^+$  is used as alkylating and protonating agents:

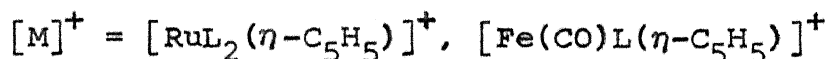
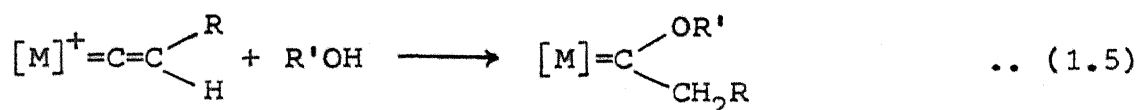


The electron distribution on the vinylidene ligand in the complex (electron deficiency on  $\alpha$ -carbon and a considerable

electron density on the  $\beta$ -carbon) renders the  $\alpha$ -carbon susceptible to nucleophilic attack and the  $\beta$ -carbon, to electrophilic attack. A few of the reactions are described below.

### Nucleophilic Addition to the $\alpha$ -Carbon

Alkoxy (alkyl) carbene complexes are formed more or less rapidly by reacting alcohols with cationic vinylidene complexes.<sup>23,38-40</sup> The addition follows the expected direction to give

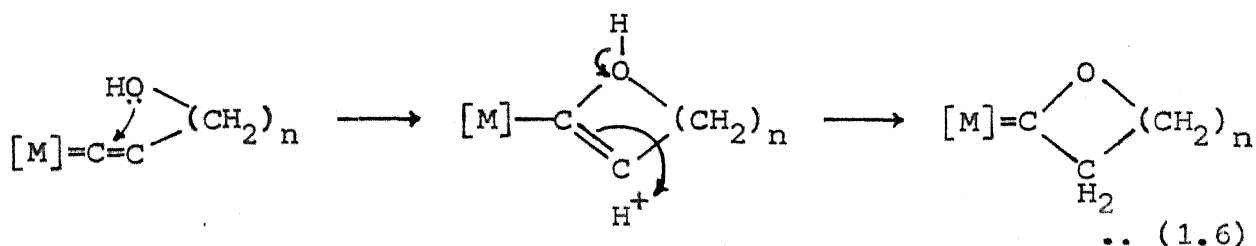


conventional Fisher type carbene complexes. It has also been observed qualitatively that the observed variation in reactivity is a combined effect of steric and electronic factors. Bulky ligands protect the  $\alpha$ -carbon from attack, and the rates of formation of the alkoxy carbene complexes are inversely proportional to the cone angle of L in  $[(\eta-C_5H_5)Ru(PPh_3)L]: CO$  (cone angle ca.  $95^\circ$ )  $\sim$   $CN Bu^t$  (ca.  $95^\circ$ )  $> P(OMe)_3$  ( $107^\circ$ )  $> PMe_3$  ( $118^\circ$ )  $> PPh_3$  ( $145^\circ$ ). A good agreement of reactivity is also found with Tolman's<sup>41</sup> electronic factors, which predict the reactivity order,  $CO > P(OMe) > (CN Bu^t) > (PPh_3) > (PMe_3)$ .

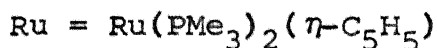
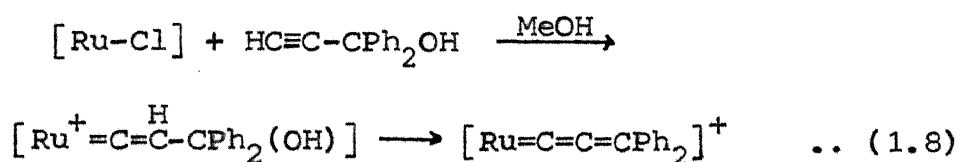
An increase in the electron-withdrawing power of the vinylidene substituents, ( $:C=CHR$ ), increases the reaction rate, as has

been found with the series,  $R = CO_2Me > Ph > Me$ . The reactivity decreases<sup>23</sup> with the nature of alcohols, viz.,  $MeOH > EtOH > Pr^iOH$ .

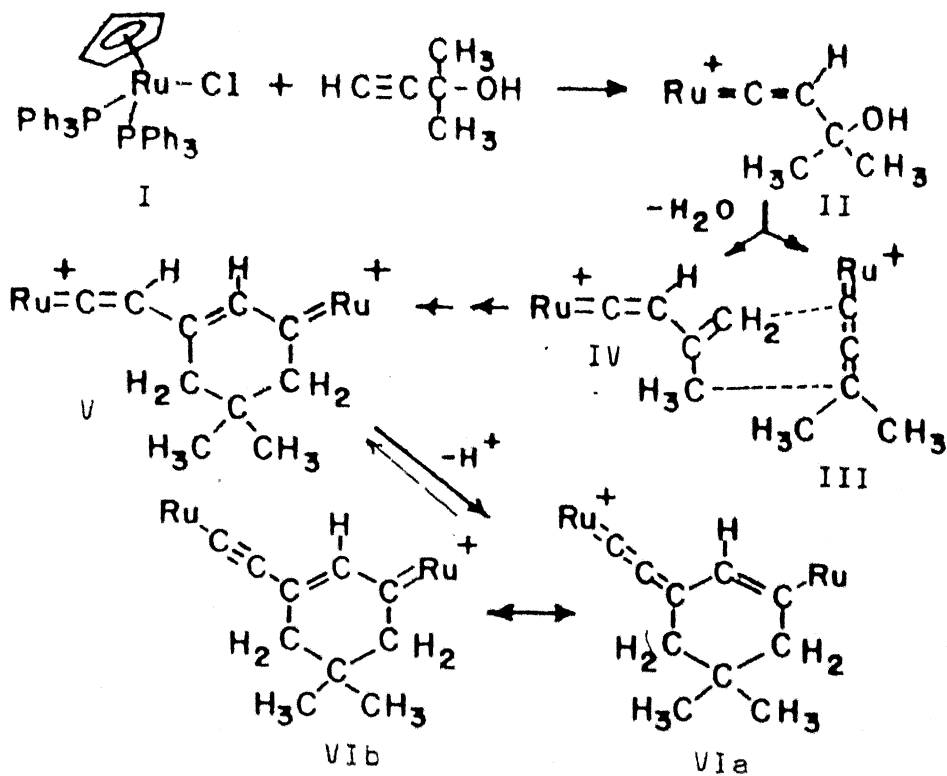
Rapid intramolecular addition of the alcohol function to a supposed intermediate vinylidene complex occurs in the reactions of  $\text{HC}\equiv\text{C}(\text{CH}_2)_n\text{OH}$  with metal halide complexes;<sup>21</sup> the cyclic carbene complexes are isolated instead:



from ynolate anions. The latter are generally obtained from reactions of alkyne complexes containing an ester group, like methylpropiolate. Vinylidene complexes containing hydroxy groups on the  $\gamma$ -carbon can be readily converted to the propadienyldiene derivative.<sup>8,9</sup> These reactions are promoted by base, or by use of  $\text{COCl}_2$  or  $\text{CSCl}_2$  for example:



Attempts to prepare the dimethyl analog from  $\text{HC}\equiv\text{CMe}_2(\text{OH})$  led to the formation of binuclear vinylidene-carbene complex  $[(\eta\text{-C}_5\text{H}_5)_2\text{-Ru}_2(\mu\text{-C}_{10}\text{H}_{12})(\text{PPh}_3)_2](\text{PF}_6)_2$ .<sup>8</sup> The pathway was described for the formation and deprotonation of the complex in the Scheme I.1. Remarkable regioselectivity is demonstrated in the formation of the two new carbon-carbon bonds. Scheme I.1 outlines a possible pathway leading to complex VI. The alkynol most probably reacts with ruthenium chloride (dissociated in methanol<sup>13,17</sup>) to give an intermediate hydroxy vinylidene complex II, which spontaneously dehydrates to a dimethylallenylidene cation III, an isopropenylvinylidene cation IV, or both. Bond formation between the two  $\delta$  carbons of IV (which should be nucleophilic at least upon deprotonation),<sup>42,43</sup> and the  $\alpha$ - and  $\gamma$ -cations of III

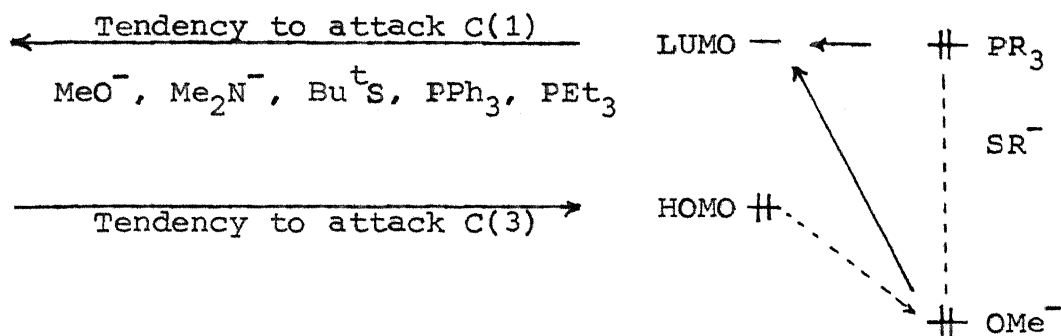


Scheme I.1

(which should be electrophilic)<sup>39,44-46</sup> probably occurs in a stepwise manner. The several requisite proton shifts should be facile in the reaction medium.

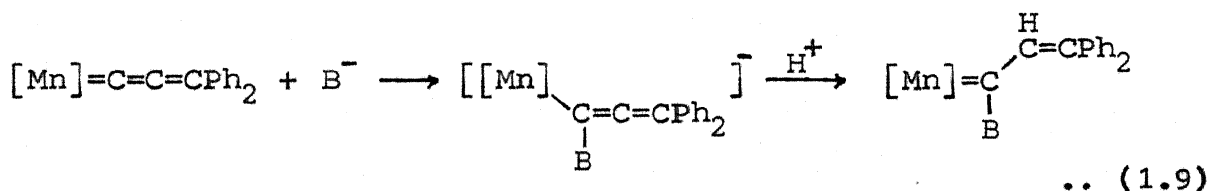
### Reactions

The reactivity of allenylidene complexes is rationalized by considering the nature of the HOMO and the LUMO of the  $\text{M}=\text{C}=\text{C}=\text{C}$  fragment.<sup>47</sup> Nucleophilic reagents can be classified according to whether they add to C(1) or C(3):

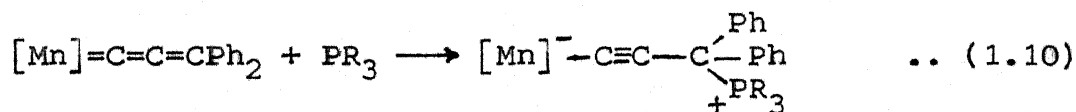


Highly electronegative donor bases (methoxide, etc.) have low-lying electron lone pairs and can interact with the HOMO, whereas tertiary phosphines have high-lying donor orbitals which interact directly with the LUMO.

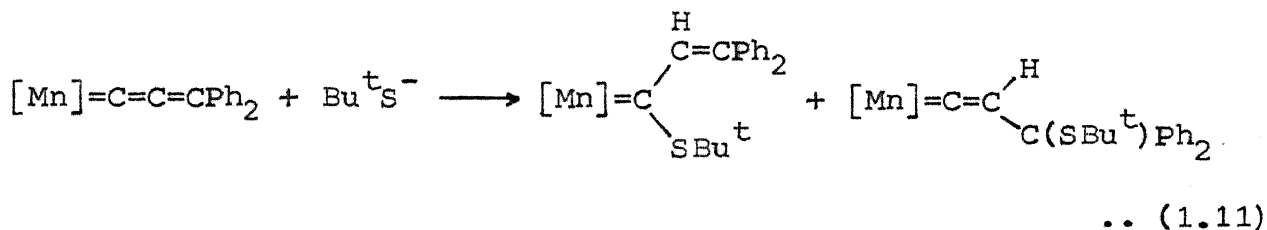
In conclusion, anionic reagents such as methoxide or amide add to C(1) and afford vinyl carbene complexes after protonation e.g.,



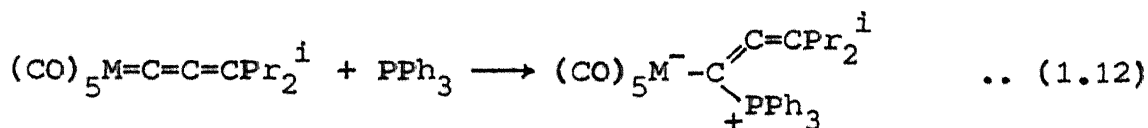
Reactions of tertiary-phosphines afford zwitterionic phosphonium salts by addition to C(3):



*t*-Butylthiolate anion attacks both the sites giving both types of products:

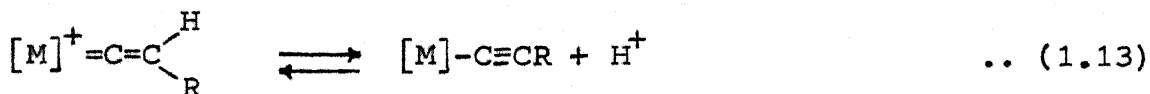


In the reactions of group VI allenylidene complexes, however, tertiary phosphines add to C(1) to give yellow complexes:<sup>48</sup>



### Synthesis of $\eta'$ -Acetylide Complexes

Cationic vinylidene complexes bearing  $\beta$ -hydrogen are rapidly deprotonated to give the corresponding neutral  $\eta'$ -acetylide complexes:



The bases used were hydroxide, alkoxide, carbonate ions, alkyl-lithium,  $\text{NaBH}_4$  or alumina.<sup>22,40,36,37</sup> The reaction is the reverse of the vinylidene synthesis by protonation of  $\eta'$ -acetylide, and the two complexes form a simple acid-base system.

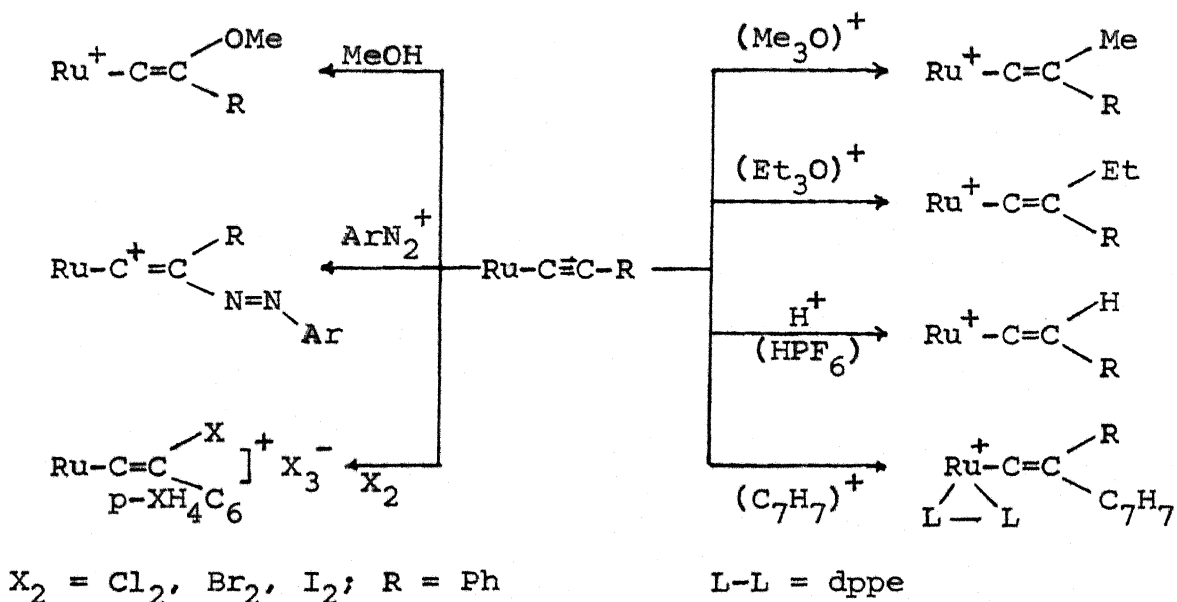
### Reactions of $\eta'$ -Acetylides, $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{C}\equiv\text{CR})]$

A wide range of complexes of the type  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)-(\text{C}\equiv\text{CR})(\text{L})]$  ( $\text{L} = \text{CO}, \text{CNBu}^t, \text{PR}_3, \text{P}(\text{OR})_3$ , etc.)<sup>22-24,49</sup> may be

synthesized by the ligand exchange reactions.

The acetylide complexes in which  $\beta$ -carbon is generally electron rich, behaves as nucleophile towards reagents such as  $H^+$ ,  $Me^+$  and  $Et^+$  (as the trialkyl oxonium salts),<sup>37,50</sup> alkyl halides,<sup>19</sup> electrophilic olefins<sup>51</sup> ( $RCH=C(CN)X$ ),  $C_7H_7^+$  and arene-diazonium salts,<sup>52</sup> yielding substituted vinylidene complexes. Halogens on reacting with  $[(\eta-C_5H_5)Ru(C\equiv CPh)(PPh_3)_2]$  readily yield halovinylidene complexes<sup>53</sup> (Scheme I.2):

Scheme I.2



( $\eta-C_5H_5$ ) and  $PPh_3$  ligands omitted from the above reactions)

$C\equiv C$  triple bond of the acetylide complexes readily forms complexes with suitable metal derivatives. Thus, copper(I) chloride forms 1:1 adducts.<sup>18,25,54</sup>



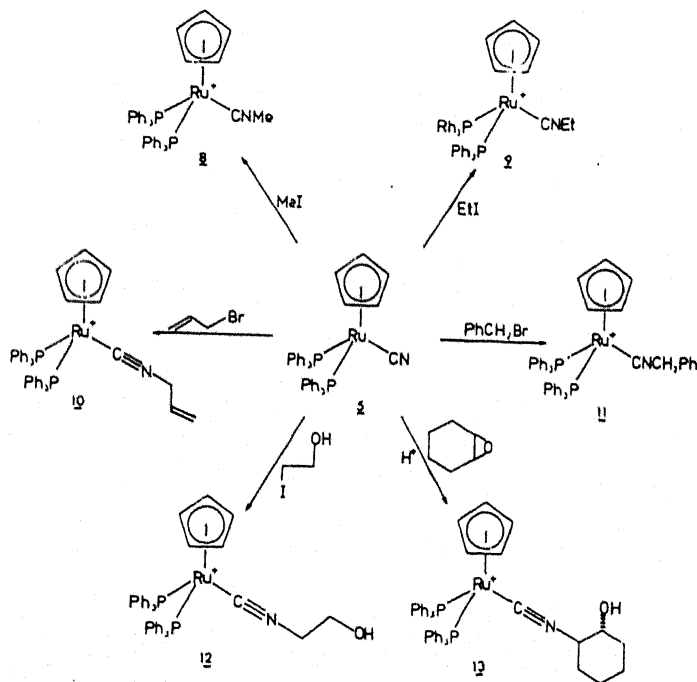


Ph; X = CN; Ar = C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-4; X = CO<sub>2</sub>Et) have shown the formation of allylic, butadienyl and in one case, cyclobutenyl complexes.<sup>51</sup> In all these cases =C(CN)X group is attached to the  $\pi$ -carbon of the acetylide.

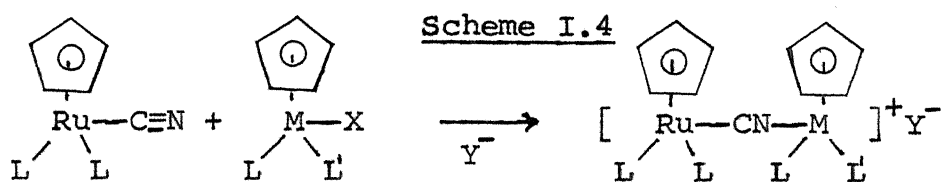
### (c) Metal-CN Bond

The cyano complex can be protonated or alkylated. It also reacts with BPh<sub>3</sub> to give  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{CNBPh}_3)]$ .<sup>13</sup> Interesting conversion from coordinated cyano group to isonitriles have been carried out by the nucleophilic reactions using RI<sup>12</sup> (R = Me, Et, CH<sub>2</sub>CHCH<sub>2</sub>, PhCH<sub>2</sub>, etc. (Scheme I.3):

Scheme I.3



Another interesting reaction of the cyano complexes is the formation of bimetallic cyano-bridged cations by treating the former with suitable organometallic halogenocomplexes  $[(\eta\text{-C}_5\text{H}_5)\text{M}(\text{LL}')\text{Cl}]$  ( $\text{M} = \text{Fe}$ ;  $\text{L}, \text{L}' = \text{dppe}$ ;  $\text{M} = \text{Ru}$ ;  $\text{L} = \text{PPh}_3$ ) (Scheme I.4):<sup>11</sup>



M	L <sub>2</sub>	L, L'	X	Y
Ru	(PPh <sub>3</sub> ) <sub>2</sub>	(PPh <sub>3</sub> ) <sub>2</sub>	Cl	PF <sub>6</sub>
Fe	(PPh <sub>3</sub> ) <sub>2</sub>	dppe	Br	PF <sub>6</sub>

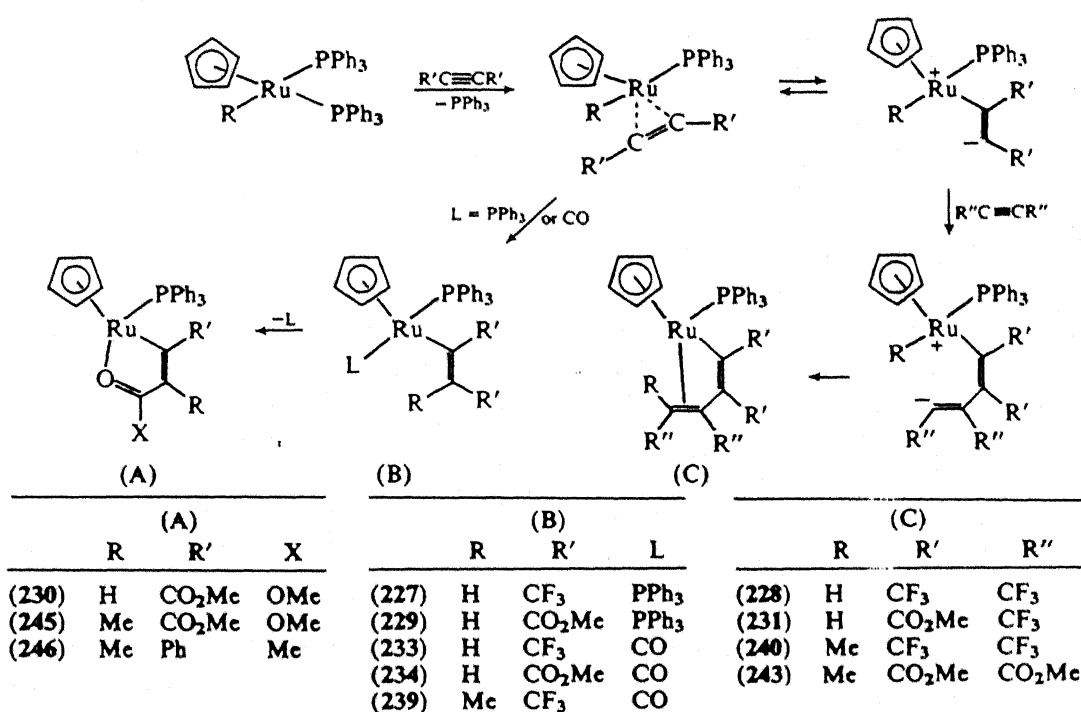
(d) Metal-R Bond (R = H or alkyl group)

The hydride complexes are generally thermally stable similar to those having  $\pi$ -acid ligands. The alkyl derivatives undergo intramolecular cyclometallation reactions by losing the alkyl group to form  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)]$ .<sup>26,29</sup>

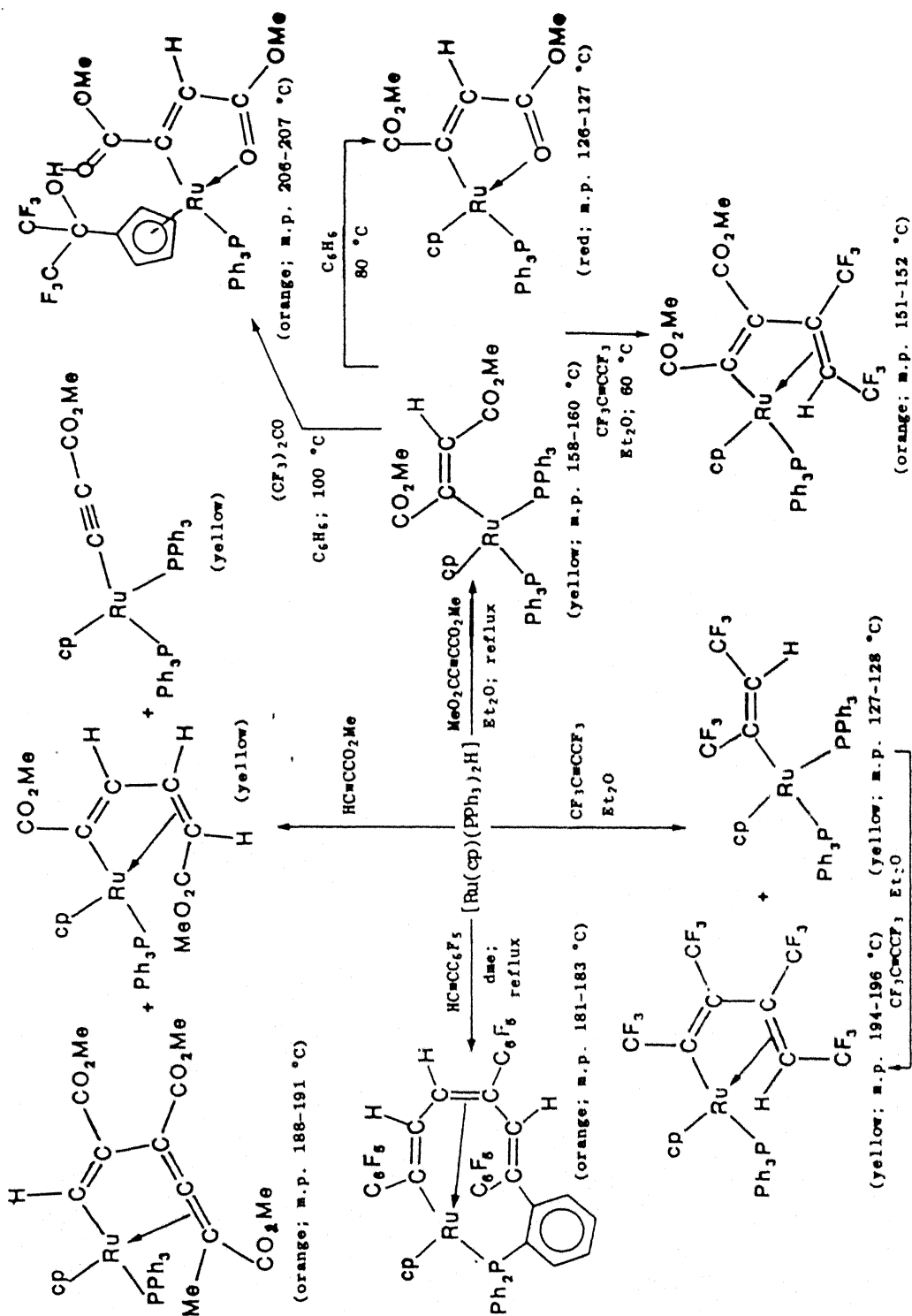
Azobenzenes, when react with alkyl complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Me}]$  readily form dark green 2-(phenylazo)phenyl complexes.<sup>29</sup> Cyclometallation by the loss of halide from an aryl group also occurs by the reaction of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Me}]$  with decafluoroazobenzene<sup>29</sup> forming a dark green complex. The reactions emphasize the attack by the electrophiles on the electron rich moiety  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2]$  which has a tendency to behave as nucleophile.

Another class of reactions belonging to this category is the ones between hydrido complex and electron deficient olefins and alkynes. These reactions yield a variety of interesting products. Thus, the reaction with  $(\text{CF}_3)_2\text{C}=\text{C}(\text{CN})_2$  gives a complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}\{\text{C}(\text{CN})_2\text{CH}(\text{CF}_3)_2\}(\text{PPh}_3)_2]$ .<sup>57</sup> Alkynes having electronegative substituents give complexes by the insertion and the cyclization process (Scheme I.5):

Scheme I.5



The reactions between terminal or substituted alkynes and the hydrido complex yield oligomeric products<sup>57, 58</sup> (Scheme I.6). In cases  $\eta'$ -acetylide derivatives are also isolated e.g., methylpropiolate.<sup>59</sup> Alkylruthenium complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{R}]$  ( $\text{R} = \text{Me}, \text{CH}_2\text{Ph}$ ) form a similarly diverse range of products in their reactions with alkynes (Scheme I.5). Several substrates



Scheme 1.6: Some Reactions of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{H}]^+$  with Alkynes

are deprotonated by the relatively basic moiety  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{Me})]$  with a loss of methane molecule.<sup>59</sup> A novel highly unsaturated alkyne trimer 1,3,4,5-tetraenyl complex<sup>58</sup> is formed by the reaction of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)\text{Me}]$  with trifluoropropyne.

In all these reactions, it is assumed that dipolar intermediates are generated by the nucleophilic attack of the electron rich  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2]$  moiety on the alkyne molecules and subsequent intra- or intermolecular process yield the observed products. Another suggested possibility for the formation of these products is the generation of an organoruthenium(IV) species, by the oxidative addition of 1-alkynes and subsequent reductive elimination (Scheme I.5).

#### 1.4 Reactions of $\text{Ru}(\eta\text{-C}_5\text{H}_5)$

The cyclopentadienyl group of the complex (I) can be readily substituted by the three monodentate ligands and particularly in the presence of oxidizing agents like NOX (X = Cl, Br, Br<sub>3</sub>) to yield Ru(II) octahedral complexes.<sup>60,61</sup> Thus, these complexes react with NOX yielding  $[\text{Ru}(\text{NO})(\text{EPh}_3)_2\text{Cl}_3]$ . The  $\text{SnCl}_3$  derivative of the complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$  yield interesting complexes<sup>61</sup>  $[\text{Ru}(\text{PPh}_3)(\text{NO}_2)\text{SnCl}_3(\eta\text{-C}_5\text{H}_5)\text{PPh}_2]$  in which one of  $\text{PPh}_3$  is  $\pi$ -bonded with ruthenium. It also reacts with SCX (X = S or O) in the presence of UV light to form mono or dithiolato complexes.<sup>62</sup> In the presence of substituted azobenzenes like decafluoroazobenzene the complex undergoes intramolecular cyclometallation

with cyclopentadienyl ring.<sup>29</sup>

### 1.5 Metal $\pi$ -Triphenylphosphine and Tetraphenylborate Sandwich Complexes

In Spectroscopy combined with X-ray crystal structure determination unravelled the mysteries of the compound  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{BPh}_4)]$ ,<sup>63</sup> obtained by the reaction of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  with  $\text{NaBPh}_4$ . The novel structure having  $\pi$ -bonded phenyl ring as proposed by IR studies<sup>63</sup> is corroborated by X-ray studies.<sup>64</sup> This has a half-sandwiched zwitterionic Ru(II) structure as shown in Fig. 1.1. Literature survey reveals several other interesting examples (Fig.1.1a,b,c,d) which fall in this category.<sup>15,65,66</sup> These compounds are unique in many ways exhibiting their own characteristic properties. They have been found to be highly useful in synthetic organic chemistry.

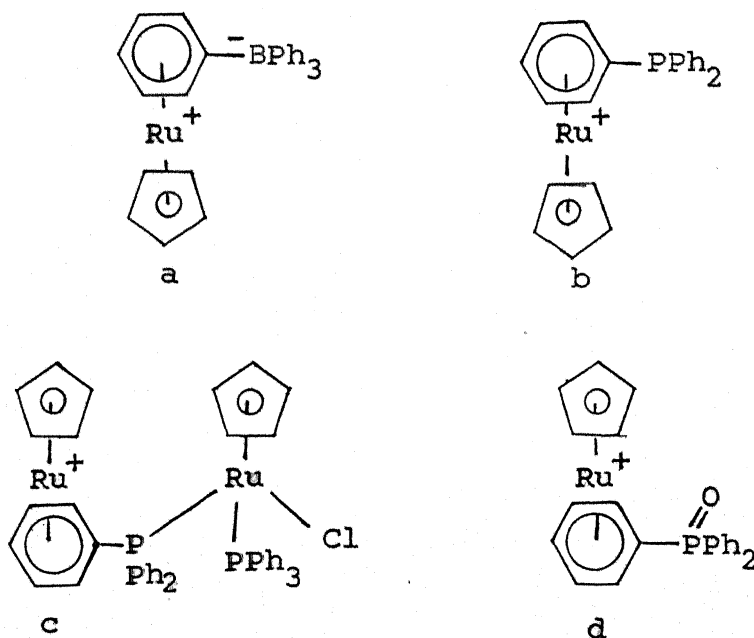


Fig. 1.1

The continued appearance of scientific papers over the past one and half decade concerning one or more aspects of this molecule and its derivatives attests, undoubtedly, the enduring importance of this complex (I) and its derivatives. An examination of literature, however, indicates that in all these reactions emphasis has been given to the reactions with unsaturated organic compounds and their derivatives resulting in the formation of some unusual  $\pi$ - and  $\sigma$ -bonded complexes.<sup>57,58,67</sup> It is thus clear from this concise review that the reactions of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{X}]$  have not only extended our horizon regarding its synthetic behaviour but have also given to chemists an opportunity for future work by providing a deeper insight into the electronic and steric factors which play an important role in these reactions.



Table I.1 Some neutral and cationic derivatives of  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru(PPh}_3)_2\text{Cl}]$

Sl. No.	Complex	Preparative Method	Ref.
1	2	3	4
1.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru(PPh}_3)_2\text{Cl}]$	$\text{RuCl}_3 \cdot x\text{H}_2\text{O} + \text{PPh}_3 + \text{C}_5\text{H}_6$ refluxed in ethanol for 2 hr.	30
2.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru(AsPh}_3)_2\text{Cl}]$	Complex 1 + $\text{AsPh}_3$ in benzene refluxed for 48 hr.	31, 28, 68
3.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru(EPh}_3)_2\text{H}]$ (E = P or As)	Compound 1/2 + NaOMe + MeOH refluxed for 15 minutes.	28
4.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru(PPh}_3)_2\text{F}]$	Compound 1 + $\text{NH}_4\text{F} + \text{NaHCO}_3$ refluxed in MeOH.	29
5.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru(PPh}_3)_2\text{X}]$ (X = Br, I, CN, NCS, etc)	Compound 1 + KX in MeOH refluxed for 1 to 3 hrs.	14, 31
6.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru(PPh}_3)_2\text{-SnCl}_3]$	Compound 1 + $\text{SnCl}_2 + 1:1$ benzene: MeOH	6, 31
7.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru(PPh}_3)_2\text{R}]$ (R = Me, $\text{CH}_2\text{Ph}$ , $\text{C}_6\text{F}_5$ , Et, $\text{Pr}^i$ )	Complex 1 in benzene + LiR in ether stirred for 45 minutes	58, 55
8.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru(CO)(PPh}_3)_2\text{-Cl}]$	Complex 1 + $\text{Fe}_2(\text{CO})_9$ in THF at $60^\circ$ stirred for 23 hr.	31
9.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru(PPh}_3)_2\text{(PMe}_3\text{)Cl}]$	1 + $\text{PMe}_3$ in light petroleum in	5, 6, 25
10.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru(PPh}_3)_2\text{(P(OPh)}_3\text{)Cl}]$	1 + $\text{P(OPh)}_3$ in decalin refluxed for 2 min.	28
11.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru(PPh}_3)_n\text{(L-L)Cl}]$ (L-L = dppm or dppe; n = 0, 1)	1 + L-L in benzene refluxed for few hours.	27

...contd.

Table I.1 (contd.)

1	2	3	4
12.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{L})(\text{PPh}_3)\text{X}]$ (L = Py, $\nu$ -pic; X = Cl, Br, I, NCS, CN & SnCl <sub>3</sub> )	1 + L refluxed in ethanol	69
13.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)\text{-(L-L)}]^+\text{Y}^-$ (L-L = bipy, o-phen, nbd, H <sub>2</sub> bim etc.; Y = PF <sub>6</sub> <sup>-</sup> , BF <sub>4</sub> <sup>-</sup> )	1 + BF <sub>4</sub> <sup>-</sup> /PF <sub>6</sub> <sup>-</sup> + L-L in EtOH refluxed for several hours	69, 65
14.	$[(\eta\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$ (L = PMe <sub>3</sub> ; P(OMe) <sub>3</sub> , P(OPh) <sub>3</sub> , PPh <sub>2</sub> Me, PPh <sub>2</sub> - (OMe), PPhMe <sub>2</sub> , PPhEt <sub>2</sub> , PPh(OMe) <sub>2</sub> , PMe(OMe) <sub>2</sub> ; L <sub>2</sub> = dppm, dppe)	1 + L <sub>2</sub> refluxed in nonpolar solvents (like benzene, toluene etc.) for several hours.	5
15.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PMe}_3)_3]^+\text{PF}_6^-$	1 + PMe <sub>3</sub> in MeCN at 60° and 110°C kept in sealed tube	26
16.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{P(OMe)}_3)_3]\text{PF}_6$	1 + P(OMe) <sub>3</sub> refluxed in decalin for 4 hr.	26
17.	$[(\eta\text{-C}_6\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{S}_2\text{C-Z})]$ (Z = OMe, OEt, -OPr <sup>n</sup> , NEt <sub>2</sub> , -N(CH <sub>2</sub> ) <sub>4</sub> , H)	1 + dtc or xanthate of alkali metal or ammonium salt in MeOH refluxed for few hours.	14, 28
18.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{LL}')\text{H}]$ (L = PPh <sub>3</sub> ; L' = CO, CNBu <sup>t</sup> , P(OMe) <sub>3</sub> ; LL' = dppe or dppm)	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{LL}')\text{Cl}] + \text{NaOMe/}$ MeOH refluxed for 10 minutes	28, 70

...contd.

Table I.1 (contd.)

1	2	3	4
19.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{L})]^+\text{PF}_6^-$ (L = $\text{ClCH}_2\text{CN}$ , $\text{CH}_2=\text{CHCN}$ , $\text{CH}_2=\text{CClCN}$ , $\text{PhCN}$ , $\text{C}_6\text{F}_5\text{CN}$ etc.)	1 + appropriate nitrile + $\text{NH}_4\text{PF}_6$ + MeOH refluxed for 1-3 hours	26
20.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{L}_{1/2}]\text{BPh}_4$ (L = $\text{NC}(\text{CH}_2)_2\text{CN}$ , 1,3- $\text{C}_6\text{H}_4$ - (CN) $_2$ , 1,4- $\text{C}_6\text{H}_4$ (CN) $_2$ , $\text{Ph}_2\text{PC}\equiv\text{CPh}_2$ )	1 + dinitrile + $\text{NaBPh}_4$ + MeOH, refluxed	26
21.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{CNR})]\text{PF}_6$ (R = $\text{CH}_2\text{Ph}$ , Me, Et, $\text{CH}_2\text{CHCH}_2$ , - $\text{CH}_2\text{CH}_2\text{OH}$ etc.)	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{CN}] + \text{RI}$ in $\text{CH}_2\text{Cl}_2$ stirred at room temperature	12
22.	$[(\eta\text{-C}_5\text{H}_5)\text{L}_2\text{Ru}(\mu\text{-CN})\text{ML}_2'] -$ $(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$ ( $\text{L}_2 = (\text{PPh}_3)_2$ or dppe; M = Fe or Ru; $\text{L}_2' = (\text{PPh}_3)_2$ dppe)	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{CN}] +$ $[\text{M}(\eta\text{-C}_5\text{H}_5)\text{L}_2'\text{X}]$ (M = Fe or Ru; $\text{L}_2' = (\text{PPh}_3)_2$ or dppe stirr- ed in MeOH at $50^\circ\text{C}$ )	11
23.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)]$	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{Me})(\text{PPh}_3)_2]$ intra molecular cyclometal- lation	29
24.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{C}_6\text{H}_4\text{OP}(\text{OPh})_2) -$ $(\text{P}(\text{OPh})_3)]$	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{P}(\text{OPh})_3)_2\text{Cl}]$ reflux in decalin	28, 29
25.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PMe}_3)_2\text{L}]\text{PF}_6$ (L = $\text{CH}=\text{CHPh}$ , $\text{CH}_2=\text{CHCN}$ , $\text{CH}=\text{CHCH}_3$ , trans- $\text{ClCH}=\text{CHCl}$ , cis- $\text{EtO}_2\text{CCH}=\text{CHCO}_2\text{Et}$ , $\text{PhC}\equiv\text{CPh}$ , $\text{EtC}\equiv\text{CEt}$ , $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ )	$[(\eta\text{-C}_5\text{H}_5)\text{RuCl}(\text{PMe}_3)_2] + \text{L}$ + $\text{NH}_4\text{PF}_6$ in MeOH refluxed, concentrated to near dryness extracted with $\text{CH}_2\text{Cl}_2$ / pet. ether	24, 22
26.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{dppe})\text{L}]\text{PF}_6$ (L = $\text{C}=\text{C}-\text{R}$ ; R = Me, Et, $\text{Pr}^n$ )	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{dppe})\text{Cl}] + \text{L} +$ $\text{NH}_4\text{PF}_6$ in MeOH	26

...contd.

Table I.1 (contd.)

1	2	3	4
27.	$[(\eta-C_5H_5)Ru(PPh_3)_2(C_2HR)]^+X^-$ (R = Me, Pr, Ph, CO <sub>2</sub> Me, C <sub>6</sub> H <sub>4</sub> F-P or C <sub>6</sub> F <sub>5</sub> ; X = PF <sub>6</sub> , BF <sub>4</sub> , BPh <sub>4</sub> )	$[(\eta-C_5H_5)Ru(PPh_3)_2Cl]$ + HC≡CR + NaBF <sub>4</sub> or NaBPh <sub>4</sub> or NH <sub>4</sub> PF <sub>6</sub> in MeOH heated under reflux for 10 min.	22
28.	$[(\eta-C_5H_5)Ru(dppm)(C_2HR)]^+X^-$ (R and X same as in 27)	$[(\eta-C_5H_5)Ru(dppm)Cl] +$ HC≡CR + NaBF <sub>4</sub> or NaBPh <sub>4</sub> NH <sub>4</sub> PF <sub>6</sub> in MeOH	22
29.	$[(\eta-C_5H_5)Ru(PPh_3)_2(C_2R)]$ (R is same as in 27)	Complex 27 + NaOMe MeOH	22
30.	$[(\eta-C_5H_5)Ru(L_2)(C_2R)]$ (L <sub>2</sub> = dppm or dppe)	28 + NaOMe in MeOH	22, 49
31.	$[(\eta-C_5H_5)Ru(L_2)(C=CRR')]^+PF_6^-$ (R = Me, Pr, CO <sub>2</sub> Me, Ph, C <sub>6</sub> H <sub>4</sub> F-P or C <sub>6</sub> F <sub>3</sub> ; R' = Me or Et; L <sub>2</sub> = (PPh <sub>3</sub> ) <sub>2</sub> or dppm)	27 or 28 + (R' <sub>3</sub> O)PF <sub>6</sub> (R' = Me or Et) in CH <sub>2</sub> Cl <sub>2</sub> stirred for 1/2 hour	23, 49
32.	$[(\eta-C_5H_5)Ru(PPh_3)(L)-$ $\{C(OR')CH_2R\}]PF_6$ (L = PPh <sub>3</sub> , CO; R = Ph, Me; R' = Me, Et)	27 + MeOH refluxed	23
33.	$[(\eta-C_5H_5)Ru(dppm)\{C(OMe)CH_2-$ Ph $\}]Cl$	$[(\eta-C_5H_5)Ru(dppm)Cl] +$ MeOH + HC≡C-Ph refluxed	23
34.	$[(\eta-C_5H_5)Ru(PPh_3)L-$ $\{C(OR')=CHR\}]$	28 + NaOMe	23
35.	$[(\eta-C_5H_5)Ru(dppm)\{C(OMe)=CHPh\}]$	34 + NaOMe in MeOH	23
36.	$[(\eta-C_5H_5)Ru(PPh_3)_2C=\overset{Br}{\underset{Br_3^-}{C}}-C_6H_4Br-P]^+$	29 + Br <sub>2</sub> in CH <sub>2</sub> Cl <sub>2</sub>	53
37.	$[(\eta-C_5H_5)Ru(PPh_3)_2C=\overset{Ph}{\underset{NNAr}{C}}]^+$	29 + ArN <sub>2</sub> <sup>+</sup> in THF	52

...contd.

Table I.1 (contd.)

1	2	3	4
38.	$[(\eta-C_5H_5)RuL_2(C\equiv CR)]$ + $CHAR=C(CN)X$ (Ar = $C_6H_4NO_2-4$ ; X = CN, $CO_2Et$ )	Forms allylic, butadienyl and cyclobutanyl complexes of cyclopentadienyl- ruthenium	51
39.	$[(\eta-C_5H_5)Ru(dppe)-$ $C \begin{array}{c} \nearrow Ph \\ \searrow C_7H_7 \end{array} ]PF_6$	$[(\eta-C_5H_5)Ru(C_2Ph)] +$ $C_7H_7^+ + NH_4PF_6$ in THF	52
40.	$[(\eta-C_5H_5)Ru(\eta-C_6H_5BPh_3)]$	1 + NaBPh <sub>4</sub> in boiling MeOH affords brown crystals	63
41.	$[(\eta-C_5H_5)Ru(\eta-C_6H_5Ph_2PO)]-$ $ClO_4$	1 + NaClO <sub>4</sub> passed O <sub>2</sub> for 45 minutes.	65
42.	$[(\eta-C_5H_5)RuCl(PPh_3)PPh_2-$ $(\eta-C_6H_5)Ru(\eta-C_5H_5)]BPh_4$	1 + ethylene glycol reflux for 1 minut	15
43.	$[(\eta-C_5H_4R)RuCl(PPh_3)PPh_2-$ $(\eta-C_6H_5)Ru(\eta-C_5H_4R)]BPh_4$ (R = Me or H)	1 + $[(\eta-C_5H_4R)Ru(PPh_3)_2Cl]$ in ethylene glycol reflux for 1 minute.	15
44.	$[(\eta-C_5H_4R)Ru(\eta-C_6H_5)PPh_2]-$ $BPh_4$ (R = H or Me)	$[(\eta-C_5H_4R)Ru(PPh_3)_2Cl]$ in ethylene glycol	15
45.	$[(\eta-C_5H_5)_2Ru]$	$[(\eta-C_5H_5)Ru(PPh_3)_2Cl] + C_5H_6$	14, 15
46.	$[(\eta-C_6H_5-PPh_2)Ru(L)NO_2-$ $SnCl_3](L = Py, \gamma-pic,$ $PPh_3)$	$[(\eta-C_5H_5)Ru(PPh_3)_2SnCl_3] +$ NOX (X = Br <sub>3</sub> , NO <sub>2</sub> ) in CH <sub>2</sub> Cl <sub>2</sub>	60, 61
47.	$[(\eta-C_5H_5)Ru(PPh_3)_2-$ $(C=CMePh)]I$	$[(\eta-C_5H_5)Ru(PPh_3)_2(C\equiv CPh)]$ and MeI	49

...contd.

Table I.1 (contd.)

1	2	3	4
	OR'		
48.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\overset{\text{OR}'}{\underset{ }{\text{-C-CH}_2\text{R}}})(\text{PPh}_3)\text{L}]$ <p>and <math>[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\overset{\text{OR}'}{\underset{ }{\text{-C=CHR}}})(\text{PPh}_3)\text{L}]</math></p> <p>(L = PPh<sub>3</sub> or CO, R, R' = alkyl or aryl)</p>	$[\text{Ru}(\eta\text{-C}_5\text{H}_5)\text{L}(\text{PPh}_3)]$ moiety have been deprotonated with NaOMe	20
49.	$[\text{Ru}(\overset{\text{CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2}{\eta^2\text{-CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2})-(\eta\text{-C}_5\text{H}_5)\text{Cl}]$	Complex 1 + 2CH <sub>2</sub> =CHC <sub>6</sub> H <sub>4</sub> -PPh <sub>2</sub> refluxed in light petroleum	71
50.	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SP})\text{H}]$ <p>(SP = 2 CH<sub>2</sub>=CHC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)</p>	$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SP})\text{Cl}] + \text{NaOMe}$ in MeOH refluxed for 1 hr	71
51.	$[(\eta\text{-C}_5\text{H}_5)\text{RuCS}_2-\{\text{CH}(\text{CH}_3)\text{C}_6\text{H}_4\text{PPh}_2\}]$	Compound 50 + CS <sub>2</sub> stirred for 2 days	71

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## Chapter II

### A. SYNTHESIS OF (CHLORO)(TRIPHENYLARSINE) ( $\eta$ -CYCLOPENTADIENYL)-RUTHENIUM COMPLEX AND ITS REACTIONS WITH N-DONOR LIGANDS

#### Introduction

The synthetic information regarding the arsine and stibine analogues of the complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{X}]$  is almost unavailable in the literature.<sup>1,2</sup> The question as to why one did not attempt in this direction is difficult to answer. Two approaches have been made by us in synthesizing these complexes. In addition, it has been found that in the phosphine analogue of the complexes only one molecule of the  $\text{PPh}_3$  is substituted by the N-heterocyclic bases<sup>3</sup> with the second molecule remaining bonded with the metal ion. Although it is possible an intermediate formulated as  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)\text{X}]$  is forming during these substitution reactions, such a species is not reported in the literature.<sup>4-6</sup> This chapter (Section A) describes our attempts in this direction and deals with the synthesis of the complex  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{AsPh}_3)\text{Cl}]$  and its reactions with N-heterocyclic bases.

## Experimental

The reagents used in the reactions were of AR or chemically pure grade. The solvents were dried and distilled before use.  $[\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{MeOH}]$  was prepared by known method.<sup>7</sup> Reactions were carried out under inert atmosphere.

### (a) Preparation of $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)\text{Cl}].3/4\text{CH}_2\text{Cl}_2$ (I)

A mixture of  $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{MeOH}$  (1 g, 1.2 mmol), cyclopentadiene (2 ml, 22.5 mmol) and zinc powder (0.1 g) in benzene (100 ml) was stirred for 15 hr at room temperature. The resulting solution was filtered and the filtrate concentrated to about 10 ml. A small amount of dichloromethane and n-hexane were added whereupon a light orange compound was precipitated out which was separated by centrifugation, crystallized from  $\text{CH}_2\text{Cl}_2$ -n-hexane, and washed repeatedly with n-hexane. The product was analysed for  $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)\text{Cl}].3/4\text{CH}_2\text{Cl}_2$ , m.p.  $102^\circ$ ; yield: 30%.

### (b) Reaction of (I) with Pyridine and $\gamma$ -picoline: Formation of $[\text{RuCl}_2(\text{AsPh}_3)(\text{Py})_2]$ and $[\text{RuCl}_2(\gamma\text{-pic})_3]$

A solution of (I) (100 mg, 0.2 mmol) in methanol (20 ml) containing pyridine/ $\gamma$ -picoline (1 ml) was refluxed for about 3 hr. The resulting mixture was centrifuged and the centrifugate concentrated to about 5 ml on a water-bath. Excess of petroleum ether ( $40\text{--}60^\circ$ ) (15-20 ml) was added to the concentrate whereby a

yellow precipitate was obtained. It was filtered and recrystallized from  $\text{CH}_2\text{Cl}_2$ -light petroleum ( $40-60^\circ$ ). The reaction product with pyridine was analysed for  $[\text{Ru}(\text{AsPh}_3)(\text{Py})_2\text{Cl}_2]$  (yield: 60%) and with  $\gamma$ -picoline for  $[\text{RuCl}_2(\gamma\text{-pic})_3]$ .

(c) Reaction of (I) with 2,2'-Bipyridyl: Formation of  $[\text{RuCl}_2(\text{AsPh}_3)_2(\text{bipy})]$  and  $[\text{Ru}_2\text{Cl}_4(\text{bipy})_3(\text{AsPh}_3)]$

To a refluxing, nitrogen purged solution of (I) (100 mg, 0.2 mmol) in methanol (20 ml), 2,2'-bipyridyl (100 mg) was added and the refluxing was continued for 4 hr. The resulting solution was concentrated to about 5 ml on a water-bath and  $\text{CH}_2\text{Cl}_2$  (2 to 3 ml) added to the concentrated solution whereby an orange red complex precipitated out. It was centrifuged, washed several times with  $\text{CH}_2\text{Cl}_2$  and dried. It was analysed for  $[\text{Ru}_2\text{Cl}_4(\text{bipy})_3(\text{AsPh}_3)]$ , (yield: 50%).

To the centrifugate excess diethyl ether was added to precipitate an orange complex, soluble in dichloromethane. It was recrystallized from  $\text{CH}_2\text{Cl}_2$ -ether. It was analysed for  $[\text{RuCl}(\text{bipy})(\text{AsPh}_3)_2]$ ; yield: 30%.

(d) Reaction of (I) with 1,10-Phenanthroline: Formation of  $[\text{Ru}_2\text{Cl}_4(\text{o-phen})_3]$  and  $[\text{Ru}_2\text{Cl}_4(\text{AsPh}_3)_2]\cdot\text{CH}_2\text{Cl}_2$

These complexes were prepared by the procedure adopted for the preparation of 2,2'-bipyridyl complexes. As in the case of 2,2'-bipyridyl complexes, the complexes  $[\text{Ru}_2\text{Cl}_4(\text{o-phen})_3]$

and  $[\text{Ru}_2\text{Cl}_4(\text{AsPh}_3)_2(\text{o-phen})_2] \cdot \text{CH}_2\text{Cl}_2$  were separated taking advantage of their solubility difference in  $\text{CH}_2\text{Cl}_2$ . The solubility of  $[\text{Ru}_2\text{Cl}_4(\text{AsPh}_3)_2(\text{o-phen})_2]$  in  $\text{CH}_2\text{Cl}_2$  was much higher as compared to that of  $[\text{Ru}_2\text{Cl}_4(\text{o-phen})_3]$ . The complexes were dried in vacuo.

### Results and Discussion

The room temperature magnetic measurements were taken by using a Guoy balance. All the compounds were found to be diamagnetic. The analytical and UV visible data are given in Table IIA.1.

The orange coloured complex (I) is stable in air and soluble in organic solvents like  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , MeOH etc. The IR spectrum of the compound in KBr matrix exhibited a moderately intense band at  $840 \text{ cm}^{-1}$  due to cyclopentadienyl moiety, besides the characteristic bands of  $\text{AsPh}_3$ . In the far IR the band at  $280 \text{ cm}^{-1}$  could be assigned to (Ru-Cl) of the bridging chloride of the complex. Its diamagnetic nature was indicative of pairing of the electrons in  $d^6$  system ( $\text{Ru}^{\text{II}}$ ). Generally such a situation is present in the octahedral complexes of ruthenium(II) and thus complex (I) is assigned the octahedral geometry.

The substitution products obtained by the reaction of (I) with N-donor bases are found to be stable in air having yellow to red colour (Table IIA.2). Except for  $[\text{Ru}_2\text{Cl}_4(\text{bipy})_3(\text{AsPh}_3)]$  and  $[\text{Ru}_2\text{Cl}(\text{o-phen})_3]$ , other substitution products are soluble in organic solvents, viz.,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , MeOH and insoluble in hydrocarbons like petroleum ether, benzene, etc.  $[\text{Ru}_2\text{Cl}_4(\text{bipy})_3\text{AsPh}_3]$

and  $[\text{Ru}_2\text{Cl}_4(\text{o-phen})_3]$  are relatively much less soluble in polar solvents. All these complexes are diamagnetic suggesting the presence of ruthenium in +2 oxidation state.

The IR spectra of all the substitution products in KBr matrix did not exhibit the characteristic cyclopentadiene band around  $820\text{ cm}^{-1}$ , suggesting the absence of this moiety in the products. The presence of bands characteristic of pyridine,  $\gamma$ -picoline, 2,2'-bipyridyl, or 1,10-phenanthroline<sup>3,7</sup> and/or  $\text{AsPh}_3$ , further indicated their formation by the replacement of cyclopentadienyl moiety by the N-donor bases.

The PMR spectra of all these complexes, except those of  $[\text{RuCl}_2(\text{bipy})_{3/2}(\text{AsPh}_3)_{1/2}]$  and  $[\text{RuCl}_2(\text{o-phen})_{3/2}]$  (due to solubility problem), were recorded in  $\text{CDCl}_3$  employing H-100 Varian instrument and TMS as internal standard. The complexes displayed a broad signal at  $\delta 8.0$  indicating the presence of  $\text{AsPh}_3$ , o-phenanthroline, pyridine and/or picoline. In the latter case another signal was also found around  $\delta 2.0$  characteristic of  $\text{CH}_3$  protons. The PMR spectrum of the complex (I) exhibited a signal at  $\delta 6.5$  (besides the one at  $\delta 8.0$  due to  $\text{AsPh}_3$ ) due to the presence of  $\pi$ -bonded cyclopentadiene. The protons of the lattice-held  $\text{CH}_2\text{Cl}_2$  in complex (I) could not be distinguished from the noise of the instrument. It was, therefore, not possible to substantiate the presence of  $\text{CH}_2\text{Cl}_2$  by PMR data.

The absorption bands in the UV-visible region of the complexes are given in Table IIA.1. Complex (I) exhibited a band



around  $16950\text{ cm}^{-1}$  which has been assigned to metal-ligand charge transfer band, a characteristic of the octahedral complexes of ruthenium(II). Since the metal ion in all the complexes is bonded to heterocyclic bases having delocalised  $\pi$ -electrons, the low spin  $d^6$ -configuration of the metal ion provides filled orbitals of the proper symmetry to interact with relatively low energy unoccupied  $\pi^*$ -orbitals of the ligands. Consequently, the electronic spectra of the substitution products, recorded in  $\text{CHCl}_3$  on a Cary-17D model spectrophotometer, exhibited two broad bands in the region  $25000$  to  $20000\text{ cm}^{-1}$  which could be attributed to metal to ligand charge transfer transition  $t_{2g} \rightarrow \pi^*$ . The energy of these transitions varied in accordance with the position of N-donor bases in the spectrochemical series. It is, however, difficult to make such a correlation because of a number of complex factors like delocalisation energy etc., on which the positions of absorption maxima depend. It is, however, quite obvious that there is a tendency for the band position to get blue-shifted from pyridines to 1,10-phenanthroline. It could be that because of the greater delocalization of  $\pi$ -electron density in 1,10-phenanthroline or 2,2'-bipyridyl,  $\pi^*$ -orbitals of the latter bases may become closer to  $t_{2g}$  orbital in energy. It will lead to the greater interaction between them ( $t_{2g}, \pi^*$ ) which might result in an increase in the value of  $\Delta E$  between ( $t_{2g} + \pi^*$ ) and ( $t_{2g} - \pi^*$ ) with concomitant shift in the band position towards blue in the bipyridyl and 1,10-phenanthroline complexes. This explanation for the blue-shift is purely tentative. The

presence of the bands in the region  $25000-1666\text{ cm}^{-1}$ , however, suggested that the ruthenium ion has an octahedral surrounding. Since these complexes are of mixed ligand type, one may expect the formation of a number of isomers of these complexes. No attempt has, been made, however, to identify the type of isomers formed during these substitution reactions.

Complex	Colour	M.P. <sup>‡</sup> (°C)	Analysis: Found (Calcd.), %					$\lambda_{\max}$ (cm <sup>-1</sup> )
			C	H	N	X	As	
$[\text{RuCl}(\text{AsPh}_3)(\eta\text{-C}_5\text{H}_5)] \cdot 3/4\text{CH}_2\text{Cl}_2$	Yellow orange	103	48.8 (49.9)	3.2 (3.7)	-	15.1 (15.5)	12.8 (13.1)	16950
$[\text{RuCl}_2(\text{AsPh}_3)(\text{Py})_2]$	Yellow	105	52.9 (52.8)	3.8 (3.9)	4.8 (4.4)	11.0 (11.2)	11.5 (11.8)	25641, 21740, 40000
$[\text{RuCl}_2(\gamma\text{-pic})_3]$	Yellow	140d	48.4 (47.9)	4.5 (4.7)	8.8 (9.3)	15.4 (15.7)	-	25641, 21978, 41067
$[\text{RuCl}_2(\text{AsPh}_3)_2(\text{bipy})]$	Orange	146d	58.1 (58.7)	4.5 (4.1)	3.5 (3.0)	7.4 (7.6)	15.8 (16.0)	25000, 21740, 34483
$[\text{RuCl}_2(\text{bipy})_{3/2}(\text{AsPh}_3)_{1/2}]$	Orange red	260d	50.8 (51.5)	4.4 (3.5)	7.4 (7.4)	11.2 (12.7)	6.2 (6.7)	22222, 23809, 34483
$[\text{RuCl}_2(\text{AsPh}_3)(\text{o-phen})] \cdot 1/2\text{CH}_2\text{Cl}_2$	Orange	214	52.8 (52.3)	4.2 (3.4)	4.6 (4.0)	15.0 (15.2)	10.1 (10.7)	21740, 24691, 37037
$[\text{RuCl}_2(\text{o-phen})_{3/2}]$	Orange red	290	48.8 (48.9)	2.5 (2.7)	9.5 (9.3)	15.6 (16.1)	-	22222, 37037, 37037

<sup>‡</sup> Melting points are uncorrected.

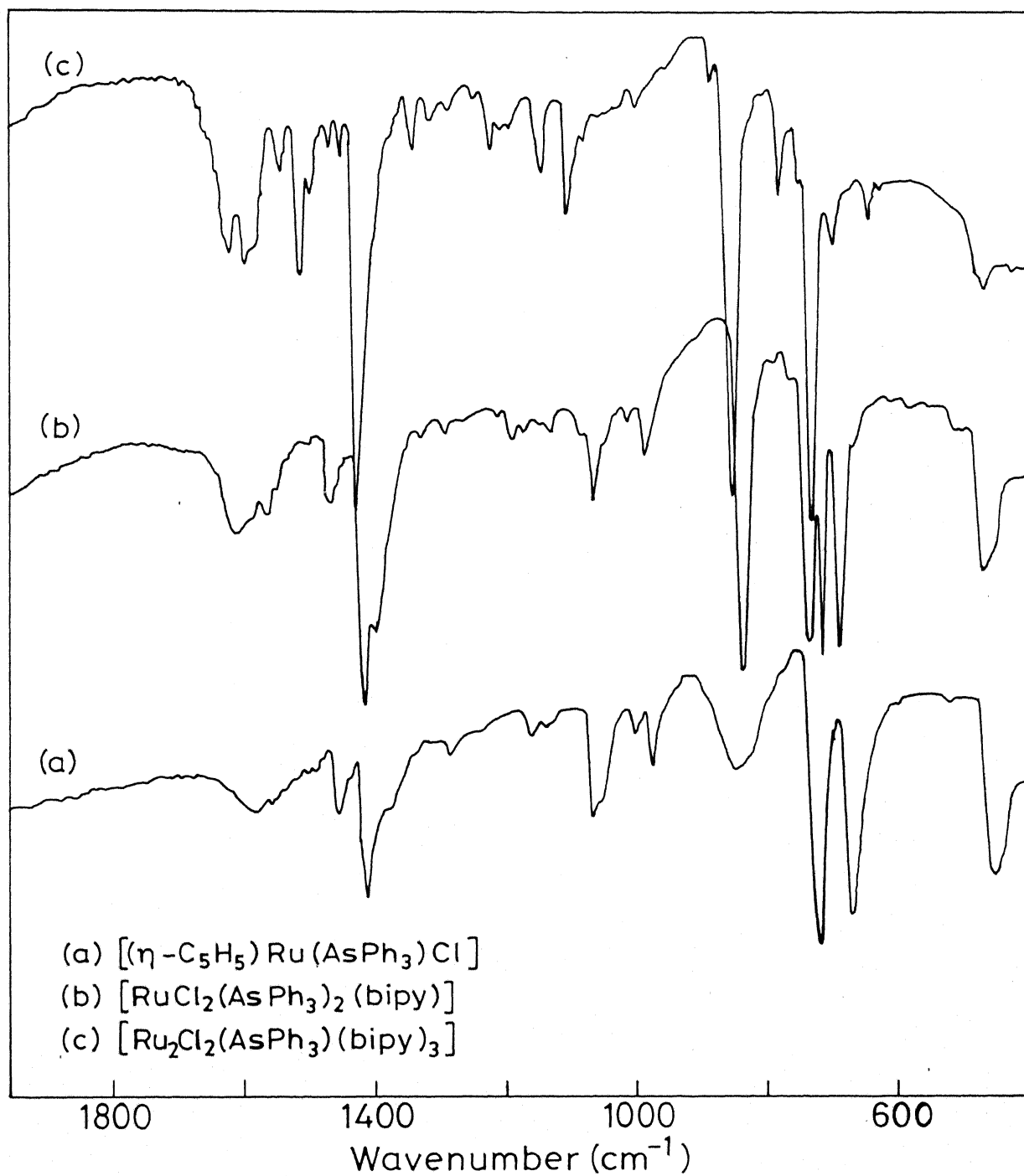


Fig. 2A.1 Infrared spectra .

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B. SYNTHESSES AND CHARACTERIZATION OF  $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)\text{LX}]$   
 AND  $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)(\text{L})(\text{MeCN})]_m^+ \text{Y}^-$  ( $\text{L} = \text{PPh}_3$  OR  $\text{AsPh}_3$ ;  
 $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{CN}, \text{H}$  OR  $\text{SnCl}_3$ ;  $\text{Y} = \text{HgCl}_3, \text{Zn}_2\text{Cl}_6$  OR  
 $\text{BPh}_4$ ;  $m = 1$  OR  $2$ )

## Introduction

The potential chemical reactivities of the complexes  $[(\eta\text{-C}_5\text{H}_5)\text{RuX}(\text{PR}_3)_2]$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ;  $\text{R} = \text{Me}$  or  $\text{Ph}$ ) with various heterocyclic bases, dienes, trienes,  $\text{NOX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{Br}_3$  or  $\text{NO}_2$ ) etc. have recently received considerable attention in the chemical literature.<sup>1-10</sup> Interest in these molecules stems from the reactions of the substitution-reaction products which they show because of the close proximity of sterically hindered two trialkyl or triaryl phosphine molecules. It has recently been demonstrated that  $[(\eta\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2]$  undergoes a substitution reaction under refluxing conditions for a very long period, giving  $[(\eta\text{-C}_5\text{H}_5)\text{RuCl}(\text{AsPh}_3)_2]$  in good yield. Since, in our previous work,<sup>8,9</sup> the substitution of one molecule of  $\text{PPh}_3$  by a heterocyclic base like pyridine has been reported, it is anticipated that substitution reactions should proceed through stepwise replacement of one molecule by another. It was, therefore, of interest to extend our investigations of substitution reactions and to attempt to synthesize mixed complexes  $[(\eta\text{-C}_5\text{H}_5)\text{RuX}(\text{A})(\text{B})]$  ( $\text{A} = \text{PPh}_3, \text{AsPh}_3$  or  $\text{SbPh}_3$ ;  $\text{B} = \text{PPh}_3, \text{AsPh}_3$  or  $\text{SbPh}_3$ ) and to interconvert them. In this chapter (Part B) we describe the

syntheses of these complexes, which have been characterized by chemical analyses, spectroscopic studies (IR, PMR and mass), the powder X-ray method, and by magnetic-susceptibility measurements.

### Experimental

All the reagents were Analar or of chemically pure grade. All the solvents were dried and distilled before use. The reactions were carried out under a dry and pure nitrogen atmosphere.  $[(\eta\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2]$ ,  $[(\eta\text{-C}_5\text{H}_5)\text{RuCl}(\text{AsPh}_3)_2]$  and  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{H}]$  were prepared by the literature methods.<sup>7,11</sup>

### Preparation of Complexes

(a) Preparation of Monochloromonocyclopentadienylmonotriphenylphosphine monotriphenylarsine ruthenium(II),  $[(\eta\text{-C}_5\text{H}_5)\text{RuCl}(\text{AsPh}_3)(\text{PPh}_3)]$  (I).

A solution of  $[(\eta\text{-C}_5\text{H}_5)\text{RuCl}(\text{PPh}_3)_2]$  (0.500 g, 0.7 mmol) and  $\text{AsPh}_3$  (0.4 g, 0.13 mmol) in 60 ml benzene was heated to reflux for 25 hr. The resulting solution was concentrated to near dryness, the residue extracted by  $\text{CH}_2\text{Cl}_2$  and the complex precipitated from the extract by using petroleum ether. It was centrifuged and purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ -petroleum ether. It was filtered, washed with petroleum ether, and dried. The orange-yellow complex I was analysed (yield: ca. 78%).

(b) Preparation of Monohydridomonocyclopentadienylmonotriphenylarsine monotriphenylphosphine ruthenium(II),  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru(AsPh}_3\text{)(PPh}_3\text{)H}]$

(i) Using NaOMe-MeOH: A mixture of the orange-yellow coloured complex I (0.1 g, 0.13 mmol) and sodium metal (0.20 g, ca. 0.009 g.atm) in 15 ml methanol was heated to reflux until all the starting material was dissolved (ca. 20 min.) with the simultaneous formation of a precipitate from the solution near the glass surface, which was separated by centrifugation, washed with small quantities of methanol, and dried in vacuo. It was identified as  $[(\eta\text{-C}_5\text{H}_5)\text{Ru(AsPh}_3\text{)(PPh}_3\text{)H}]$  by analyses (yield: ca. 50%).

(ii) Using NaOEt-EtOH: The hydrido derivative was also prepared by the same procedure as given in (b)(i), except that ethanol (15 ml) was used in place of methanol. The yellow complex was collected and identified by chemical analyses and by comparing it with that prepared in (b)(i). Both samples were found to be identical.

(c) Preparation of Mono(fluoro, bromo or iodo)monocyclopentadienylmonotriphenylarsine monotriphenylphosphine ruthenium(II),  $[(\eta\text{-C}_5\text{H}_5)\text{Ru(AsPh}_2\text{)(PPh}_3\text{)X}]$  (X = F, Br or I)

(i) Using HX (X = F, Br or I): A yellow suspension of  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru(AsPh}_3\text{)(PPh}_3\text{)H}]$  (0.1 g, 0.14 mmol) in methanol (15 ml) was treated with concentrated HX (five or six drops). Immediately,



the yellow suspension dissolved to form a light yellowish-orange coloured solution which was stirred for about 10 min, whereby a brownish-orange precipitate deposited. It was collected by centrifuging the solution, washed with methanol and ether, and dried in vacuo. On analysis it was identified as  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru(AsPh}_3\text{)(PPh}_3\text{)X}]$  (yield: ca. 90%).

(ii) Using KX (X = Br or I): Complexes of  $[(\eta\text{-C}_5\text{H}_5)\text{RuX(AsPh}_3\text{)(PPh}_3\text{)}]$  (X = Br or I) were also prepared by heating under reflux a solution of  $[\text{RuCl(AsPh}_3\text{)(PPh}_3\text{)(}\eta\text{-C}_5\text{H}_5\text{)}]$  (0.1 g, 0.13 mmol) in ethanol (20 ml) with KX (0.200 g, ca. 0.17 mol) for 1 hr, whereupon brownish-orange crystals were deposited. These were separated by centrifuging the solution, washed with water, methanol and diethyl ether, and dried. On analysis the complex was identified as  $[(\eta\text{-C}_5\text{H}_5)\text{Ru(AsPh}_3\text{)(PPh}_3\text{)X}]$  (X = Br or I) (yield: ca. 80%).

(iii) Using MeI: The iodo analogue of the complex was prepared by the procedure described in (c)(i) by treating  $[(\eta\text{-C}_5\text{H}_5)\text{Ru(AsPh}_3\text{)(PPh}_3\text{)H}]$  (0.1 g, 0.14 mmol) with methyl iodide (five or six drops) in methanol (10 ml). The resulting complex was identified as  $[(\eta\text{-C}_5\text{H}_5)\text{Ru(AsPh}_3\text{)(PPh}_3\text{)I}]$ .

(iv) The bromo analogue  $[(\eta\text{-C}_5\text{H}_5)\text{Ru(AsPh}_3\text{)(PPh}_3\text{)Br}]$  was also prepared by heating to reflux a solution of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru(PPh}_3\text{)}_2\text{Br}]$  (0.1 g, 0.12 mmol) in ethanol (30 ml) with AsPh<sub>3</sub> (0.1 g, 0.33 mmol)

for 15 h, whereupon brown crystals were deposited. These were separated by centrifuging the suspension, washed with ethanol, diethyl ether and petroleum ether. The complex was dried and identified as the bromo derivative (yield: ca. 70%).

(d) Preparation of Monocyclopentadienylmonotriphenylarsine monotriphenylphosphinetrichlorotin ruthenium(II),  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru(AsPh}_3\text{)(PPh}_3\text{)SnCl}_3\text{)]}$

A mixture of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru(AsPh}_3\text{)(PPh}_3\text{)Cl}]$  (0.1 g, 0.13 mmol) and tin(II) chloride (0.05 g, 0.25 mmol) was heated to reflux in 15 ml of benzene to which 20 ml of methanol was added. After about half an hour yellow crystals had appeared, which were separated by centrifugation. The centrifugate was further concentrated by heating on a water bath whereby more compound appeared in the concentrate. It was centrifuged, recrystallised from  $\text{CH}_2\text{Cl}_2$ -petroleum ether, washed with petroleum ether, and dried in vacuo. The complex was identified as  $[(\eta\text{-C}_5\text{H}_5)\text{Ru(AsPh}_3\text{)-(PPh}_3\text{)SnCl}_3]$  (yield: ca. 60%).

(e) Preparation of monocyanomonocyclopentadienylmonotriphenylarsine monotriphenylphosphine ruthenium(II),  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru(AsPh}_3\text{)(PPh}_3\text{)(CN)}]$

A mixture of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru(AsPh}_3\text{)(PPh}_3\text{)Cl}]$  (0.1 g, 0.13 mmol) and excess KCN (0.2 g, 0.33 mmol) was heated under reflux for 4-5 hr in methanol (20 ml), whereupon greenish-yellow

crystals separated, which were centrifuged. The centrifugate was further concentrated, yielding more of the complex as precipitate. The complex was centrifuged, washed with water, methanol and ether, and dried in vacuo. It was identified as  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{CN}]$  (yield: ca. 50%).

(f) Preparation of monocyclopentadienylmonotriphenylarsine monotriphenylphosphineacetonitrile ruthenium(II) cationic salts  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)(\text{MeCN})]^+\text{X}^-$  ( $\text{X} = \text{BPh}_4, \text{HgCl}_3$  or  $\text{Zn}_2\text{Cl}_6$ )

(i) Tetraphenylborate salt: Addition of sodium tetraphenylborate (0.05 g, 0.11 mmol) to a solution of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{Cl}]$  (0.07 g, 0.1 mmol) in 20 ml acetonitrile, followed by heating for about 20 min. under reflux, yielded a yellow solution, which was filtered. The filtrate was concentrated to nearly one-third of the volume (5 ml). Ether was then added to the concentrate, whereby the complex precipitated. It was then centrifuged and recrystallized from acetonitrile-ether. It was washed with ether and dried in vacuo. The complex was identified as  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)(\text{MeCN})]\text{BPh}_4$ .

(ii) Trichloromercurate salt: The reaction was carried out by a procedure similar to that described in (f)(i) except that mercury(II) chloride was used instead of sodium tetraphenylborate to obtain  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)(\text{MeCN})]\text{HgCl}_3$ .

(iii) Hexachlorodizincate salt: The reaction carried out by a procedure similar to that described in (f)(i) except that zinc(II) chloride was used instead of tetraphenylborate to obtain  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)(\text{MeCN})]_2\text{Zn}_2\text{Cl}_6$ .

The corresponding  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{X}]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}$  or  $\text{SnCl}_3$ ) complexes have also been prepared using same procedures as described in the above sections. In the case of chloride the refluxing time was a little more ( 24 hr.).

#### Interconversions (Scheme II-B.1)

##### Conversion of $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{Cl}]$ to $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{Cl}]$ :

A mixture of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{Cl}]$  (prepared by a method described elsewhere)<sup>13</sup> (0.1 g, 0.11 mmol) and triphenylarsine (0.1 g, 0.33 mmol) was refluxed in 20 ml benzene for 12 hr. The resulting orange solution was evaporated to dryness and the residue extracted with 10 ml of dichloromethane. Excess petroleum ether was added to the extract to give the corresponding arsine complex. It was identified by comparing its spectral and analytical data with those of the authentic sample, and by determining the mixed melting point.

##### Conversion of $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{Cl}]$ to $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$

A mixture of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{Cl}]$  (0.1 g, 0.11 mmol) and triphenylphosphine (0.1 g, 0.38 mmol) was refluxed in 20 ml of ethanol for 10 hr. The resulting solution was evaporated to

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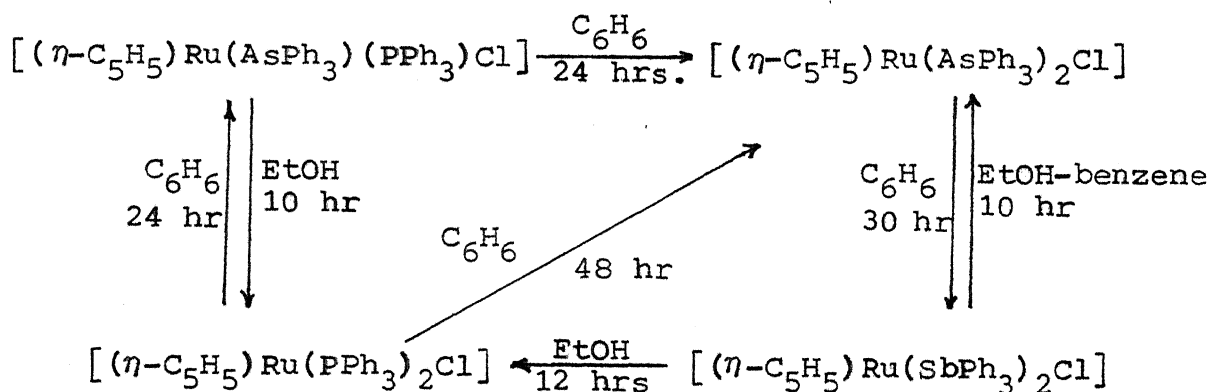
nearly 5 ml, whereby an orange crystalline precipitate appeared. It was centrifuged, washed with ethanol, recrystallized from  $\text{CH}_2\text{Cl}_2$ -petroleum ether, and dried in vacuo. The complex was identified as  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ .

Conversion of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{Cl}]$  to  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$

A mixture of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{Cl}]$  (0.1 g, 0.13 mmol) and triphenylphosphine (0.1 g, 0.40 mmol) was refluxed in 20 ml ethanol for 12 hr. The resulting solution was filtered and the filtrate was concentrated to 5 ml, whereby an orange crystalline precipitate appeared. It was filtered, washed with ethanol and diethyl ether, and dried in vacuo. The complex was identified as  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ .

Conversion of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{Cl}]$  to  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{Cl}]$

A mixture of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{Cl}]$  (0.5 g, ca. 0.65 mmol) and triphenylarsine (0.2 g, 0.64 mmol) was refluxed in benzene (20 ml) for 24 hr. The solution was then centrifuged and the centrifugate evaporated to near dryness. The residue was extracted with  $\text{CH}_2\text{Cl}_2$ , and excess petroleum ether was added to the extract to yield a crystalline product which was identified as  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{Cl}]$ .



Scheme II-B.1: Interconversion of various complexes.

### Physical Measurements

Carbon, hydrogen and nitrogen analyses were carried out by the Microanalytical laboratory of the I.I.T., Kanpur, India. The percentage of halide in the sample was determined by the standard method<sup>12</sup> in the filtrate obtained after fusing the sample with the fusion mixture (NaOH:NaNO<sub>3</sub>, 8:1), extracting it with distilled water and filtering it. IR, UV and visible, <sup>1</sup>H NMR, <sup>31</sup>P NMR and mass spectra, magnetic measurements and powder X-ray data were determined by the methods described elsewhere.<sup>13</sup> The results are given in Table II-B.1. All the complexes were found to be diamagnetic. The molecular weight of complex I was determined using a Knauer vapour pressure osmometer.

### Results and Discussion

The analytical data of the yellowish-orange, air-stable

complex I and other substitution products suggested their formula to be  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{X}]$ . Complex I was obtained as a result of the substitution reaction of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  with triphenylarsine. It was found to be highly soluble in  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  partially soluble in ethanol, methanol and diethyl ether, and insoluble in petroleum ether and n-hexane. This formulation was further confirmed by the results of the following experiments:

(i) Its experimentally determined molecular weight (752) by osmometer as against the theoretical value of 770.

(ii) By the presence of peaks in its mass spectrum with  $m/z$  values of 305, 262 and 201, corresponding to  $\text{AsPh}_3$ ,  $\text{PPh}_3$  and  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{Cl})]$ , respectively. (Since the purpose of this study was just to detect the presence of  $\text{AsPh}_3$  and  $\text{PPh}_3$  fragments, no attempt has been made to explain other relatively less intense peaks.)

(iii) Complex 1 was objected to substitution reactions which led to the scission of the Ru-Cl bond and yielded  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{X}]$  as substituted products ( $\text{X} = \text{Br}, \text{I}, \text{F}, \text{CN}$  or  $\text{SnCl}_3$ ) (Table II-B.1).

(iv) Reactions between complex 1 and zinc or mercury(II) chloride in acetonitrile produced a rapid colour change from orange to yellow of the solution from which stable yellow complexes were isolated. They were initially thought to be

1:1 adducts of the Ru complex acting as a Lewis base. Further investigations revealed that the products were salts of the cation  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)(\text{MeCN})]^+$ . The cationic nature has been tested by ion exchange studies.

It has been observed that, by refluxing a solution of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{Cl}]$  with either  $\text{PPh}_3$  or  $\text{AsPh}_3$ , it was possible to convert them to the known compounds  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{Cl}]$  ( $\text{E} = \text{P}$  or  $\text{As}$ ). These reactions have been further extended and the  $\text{PPh}_3$  or  $\text{AsPh}_3$  can easily be substituted by triphenylstibine ( $\text{SbPh}_3$ ) simply by refluxing the solution of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{Cl}]$  ( $\text{E} = \text{P}$  or  $\text{As}$ ) with  $\text{SbPh}_3$ . It has, however, been observed that the time of refluxing for the substitution reaction of the complex having  $\text{PPh}_3$  as a coligand with  $\text{AsPh}_3$ , was much longer compared to the complex having a  $\text{AsPh}_3$  as coligand. This could possibly be due to the similarity of some of the chemical properties of the alternature elements in a group.<sup>14</sup> This is, however, a tentative explanation.

The properties of the substitution products of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{Cl}]$  and  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)(\text{MeCN})]^+$  are given in Table II-B.1. Their formulae have been assigned on the basis of the chemical analyses and other properties discussed below.

### IR Spectra

The IR spectra of all the complexes exhibited two bands of



medium intensity in the  $840\text{--}850\text{ cm}^{-1}$  and  $420\text{ cm}^{-1}$  regions, corresponding to the C-H out-of-plane and skeletal bending modes of the  $\text{C}_5\text{H}_5$  ring, respectively besides the characteristic bands<sup>15</sup> of triphenylphosphine and triphenylarsine ( $1490$ ,  $1440$ ,  $1100$ ,  $750$ ,  $700$  and  $535\text{ cm}^{-1}$ ). Since the band positions due to the phenyl groups of  $\text{AsPh}_3$  and  $\text{PPh}_3$  in their IR spectra do not appreciably vary it was difficult to distinguish the presence of both triphenylarsine and triphenylphosphine in the same complexes by the IR spectra. However, it has been observed that all the phenyl bands in the IR spectra of the complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{X}]$  were relatively broader compared to those found in  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$  ( $\text{E} = \text{P}$  or  $\text{As}$ ). This broadness could possibly be taken tentatively as evidence for the presence of both  $\text{AsPh}_3$  and  $\text{PPh}_3$  in the complexes, as indicated by other experiments. The IR spectra of all the complexes displayed a characteristic pattern of three bands decreasing in intensity from  $535$  to  $495\text{ cm}^{-1}$ , which suggests the presence of a triphenylphosphine- or triphenylarsine-coordinated ligand.<sup>16</sup> Spectra of the cyanato and hydrido complexes exhibited medium intensity, slightly broad bands at  $2050$  and  $1950\text{ cm}^{-1}$ , assigned to  $\nu(\text{CN})$  and  $\nu(\text{Ru-H})$ , respectively,<sup>7,8,17</sup> confirming the presence of a  $\text{CN}^-$  or  $\text{H}^-$  ion bonded to ruthenium in the complexes.

It is interesting to observe that the  $\nu(\text{CN})$  band in all complexes having a coordinated isonitrile around  $2100\text{ cm}^{-1}$  is very weak. A low value of the transition moment is usually

observed in these type of complexes.<sup>18,19</sup> In the 400-200  $\text{cm}^{-1}$  region bands assignable to  $[\text{Zn}_2\text{Cl}_6]^{2-}$  and  $[\text{HgCl}_3]^-$  anions, besides those due to  $\nu(\text{Ru-Cl})$ , have been observed. In the spectrum of the mercury derivative a band at 285  $\text{cm}^{-1}$ , assigned to the asymmetric mode in  $[\text{HgCl}_3]^-$ , and for the zinc complex the characteristic bands of  $[\text{Zn}_2\text{Cl}_6]^{2-}$  at 335, 305, 252 and 242  $\text{cm}^{-1}$ , were present. The positions and relative intensities of the  $[\text{Zn}_2\text{Cl}_6]^{2-}$  bands were found to be similar to those observed in the IR spectra of the solutions of the complexes  $\text{B}^+\text{MCl}_3$  (B = bipy-BPh<sub>2</sub>; M = Zn or Hg), where it has been suggested<sup>20</sup> that the zinc is present as the bridged  $[\text{Zn}_2\text{Cl}_6]^{2-}$  rather than the mononuclear  $[\text{ZnCl}_3]^-$  anion.<sup>21</sup>

### <sup>1</sup>H NMR Spectra

<sup>1</sup>H NMR spectra of all the complexes showed a sharp resonance in the  $\delta$  4.0-4.5 region. The sharp singlet in this region is characteristic of  $\pi$ -bonded cyclopentadiene. The aromatic group on the triphenylphosphine and triphenylarsine ligands showed broad complex resonances in the usual range  $\delta$  7.0-8.0 for the  $\text{C}_6\text{H}_6$  protons. The integrated intensity ratio of the signals of  $\text{C}_5\text{H}_5$  and  $\text{EPh}_3$  (E = P or As) (1:6) corresponded to the ratio of the number of hydrogen atoms of the cyclopentadienyl anion and the sum of those present in triphenylphosphine and triphenylarsine. It was reported earlier that a sharp resonance in the NMR spectra of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  and

$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{Cl}]$  appears at  $\delta$  4.0 and 4.2 (Fig. 2B.2), respectively.<sup>1</sup> The presence of a peak at  $\delta$  4.1 in the complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{Cl}]$ , therefore, suggests the environment of the cyclopentadienyl protons to be different from that in the former two complexes. Furthermore, the presumption that the complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{Cl}]$  is a 1:1 mixture of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  and  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{Cl}]$  is also not tenable because of the fact that the NMR spectra of the mixture is expected to exhibit two independent peaks due to cyclopentadienyl protons at  $\delta$  4.0 and 4.2 one for each component of the mixture. The presence of only one sharp peak at  $\delta$  4.1 suggests only one type of electronic environment around the cyclopentadienyl protons. Further, the spectra of all the complexes showed a broad multiplet in the region of  $\delta$  7.8 different from the one present in the spectra of triphenylphosphine and triphenylarsine complexes. The spectra of latter two together did not match the one of complex 1 in the region of  $\delta$  7.0, indicating again that it is not a mixture of the phosphine and arsine complexes. In the case of the acetonitrile complexes, an additional signal in the  $\delta$  1.8-2.0 region was observed for the methyl protons.

<sup>31</sup>P NMR exhibited a sharp resonance at  $\delta$  39.01, indicating the presence of at least one triphenylphosphine molecule in our complex. The literature indicates one single sharp <sup>31</sup>P signal in  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  at  $\delta$  38.6, indicating the presence of two symmetrical triphenylphosphine molecules.<sup>22</sup> The shifting

of the signal in our complex towards a lower value by about  $\delta 0.5$  suggests that triphenylphosphine in our complex has different surroundings than in  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ . These data, along with those of other physical measurements, further confirm the formula to contain one molecule each of triphenylphosphine and triphenylarsine.

### Magnetic Moments and Electronic Spectra

All the complexes were found to be diamagnetic, indicating spin pairing. The symmetry of the donor atoms around the metal centre in all these complexes may be considered to be distorted octahedral, based upon the assumption that the cyclopentadienyl group occupies three coordinate sites, or distorted tetrahedral if the perpendicular axis of the  $\text{C}_5$ -ring is considered to occupy one position. The diamagnetism of the complexes is, however, strongly suggestive of the former alternative, because of the definite possibility of there being spin-free complexes in a tetrahedral environment.

The position of the absorption bands shown in the UV and visible region of the electronic spectra of complex 1 were at 375 nm and a shoulder at 455 nm due to a  $\text{M} \rightarrow \text{L}$  charge-transfer band. When we compared complex 1 with the  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  complex the absorption band showed red shifts.

The powder X-ray photograph of complex 1 is found to be identical to that of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  and  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{Cl}]$

as far as peak positions are concerned. However, the peak intensities were different from those of the phosphine and arsine analogues as expected because of the difference in the scattering power of P and As. It suggests that these three complexes are isomorphous and the same structure may be assigned to the complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{Cl}]$  as to  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ .

### Conclusions

From the above discussion it is postulated that, during the substitution reaction of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  by  $\text{AsPh}_3$  to yield  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{Cl}]$  the phosphine molecules are not both simultaneously substituted by two molecules of triphenylarsine, but the reaction proceeds by a stepwise mechanism with the formation of a stable intermediate complex having one molecule of phosphine and one molecule of arsine as ligands. Various derivatives of the  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{X}]$  ( $\text{X} = \text{Br}, \text{I}, \text{CN}$  or  $\text{SnCl}_3$ ) have been prepared and characterized. Their structures are assumed to be the same as those of their respective phosphine analogues. Although it has also been observed that phosphine, arsine and stibine analogues of the complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{Cl}]$  ( $\text{E} = \text{P}, \text{As}$  or  $\text{Sb}$ ) can be interconverted simply by refluxing the complex with the appropriate compound ( $\text{EPh}_3$ ), the substitution of phosphine or stibine involves a much shorter time of refluxing compared to that of arsine.

	Complex (molecular weight)	M.p. <sup>a</sup> (°C)	Colour <sup>b</sup>	Analysis [found (calc.)] (%)				IR bands (cm <sup>-1</sup> ) (C <sub>3</sub> H <sub>5</sub> )	C <sub>3</sub> H <sub>5</sub> <sup>1</sup> H NMR [δ (ppm)] <sup>c</sup>
				C	H	N	X/S		
1	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> )(PPh <sub>3</sub> )Cl] (770)	140d	YO	63.1 (63.8)	4.8 (5.1)	—	5.0 (4.6)	843	4.10
2	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> )(PPh <sub>3</sub> )F] (753)	138d	YO	65.5 (65.3)	4.2 (4.6)	—	—	843	4.10
3	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> )(PPh <sub>3</sub> )Br] (814)	145d	B	62.3 (60.4)	3.4 (4.3)	—	10.0 (9.8)	843	4.15
4	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> )(PPh <sub>3</sub> )I] (861)	150d	OR	57.2 (57.1)	4.3 (3.7)	—	13.4 (14.6)	843	4.12
5	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> )(PPh <sub>3</sub> )H] (735)	135d	Y	66.4 (66.9)	5.2 (4.9)	—	—	845, 1950 ν(Ru—H)	4.10
6	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> )(PPh <sub>3</sub> )SnCl <sub>3</sub> ] (959)	198	YO	51.4 (51.2)	3.6 (3.6)	—	12.0 (11.1)	840	4.45
7	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> )(PPh <sub>3</sub> )CN] (760)	240	YG	65.5 (66.3)	4.1 (4.6)	2.3 (1.9)	—	845, 2050 ν(CN)	4.45
8	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> )(PPh <sub>3</sub> )(MeCN)]BPh <sub>4</sub> (1104)	140d	YG	73.2 (72.8)	5.6 (5.2)	1.5 (1.3)	—	850	—
9	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> )(PPh <sub>3</sub> )(MeCN)]HgCl <sub>3</sub> (1894)	145d	YG	47.5 (47.7)	4.1 (3.5)	1.5 (1.3)	10.6 (9.8)	850	—
10	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> )(PPh <sub>3</sub> )(MeCN)] <sub>2</sub> Zn <sub>2</sub> Cl <sub>6</sub> (797)	180	YG	55.4 (54.5)	4.5 (4.0)	1.7 (1.5)	11.9 (11.3)	850	—
11	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> ) <sub>2</sub> F] (858)	140d	BR	62.3 (61.7)	5.0 (4.4)	—	—	840	4.10
12	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> ) <sub>2</sub> Br] (905)	146d	B	58.0 (57.2)	3.6 (4.0)	—	10.6 (9.3)	840	4.20
13	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> ) <sub>2</sub> I] (1003)	152	OR	55.2 (54.4)	3.5 (3.8)	—	13.5 (14.0)	840	4.20
14	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> ) <sub>2</sub> SnCl <sub>3</sub> ] (804)	203–205	OY	49.8 (49.1)	3.6 (3.4)	—	11.2 (10.6)	840	4.50
15	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> ) <sub>2</sub> CN] (1148)	250	YG	63.2 (62.7)	4.5 (4.3)	2.1 (1.7)	—	843, 2050 ν(CN)	4.50
16	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> ) <sub>2</sub> (MeCN)]BPh <sub>4</sub> (1125)	138	YG	71.0 (70.3)	5.4 (5.0)	1.5 (1.2)	—	850	—
17	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> ) <sub>2</sub> (MeCN)]HgCl <sub>3</sub> (1982)	148	YG	46.2 (45.8)	4.5 (3.4)	1.6 (1.2)	11.0 (9.5)	850	—
18	[(η-C <sub>3</sub> H <sub>5</sub> )Ru(AsPh <sub>3</sub> ) <sub>2</sub> (MeCN)] <sub>2</sub> Zn <sub>2</sub> Cl <sub>6</sub> (1982)	180	YG	52.5 (52.1)	4.2 (3.5)	1.6 (1.4)	12.1 (10.7)	850	—

<sup>a</sup>d = decomposition.

<sup>b</sup>YO = yellowish-orange, B = brown, OR = orange-red, Y = yellow, YG = yellowish-green, BR = brick-red.

<sup>c</sup>Solvent CDCl<sub>3</sub>. Aromatic protons of the other coligands appeared in the region of δ 7–8 as broad multiplets, and in the case of acetonitrile additional signals in the δ-1.8–2.0 region were observed due to the methyl protons.

## IR SPECTRA OF THE COMPLEXES

Fig. 2B.1 (a)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{F}]$

(b)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{Br}]$

(c)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{H}]$

Fig. 2B.2 (a)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{SnCl}_3]$

(b)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{CN}]$

(c)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{NCS}]$

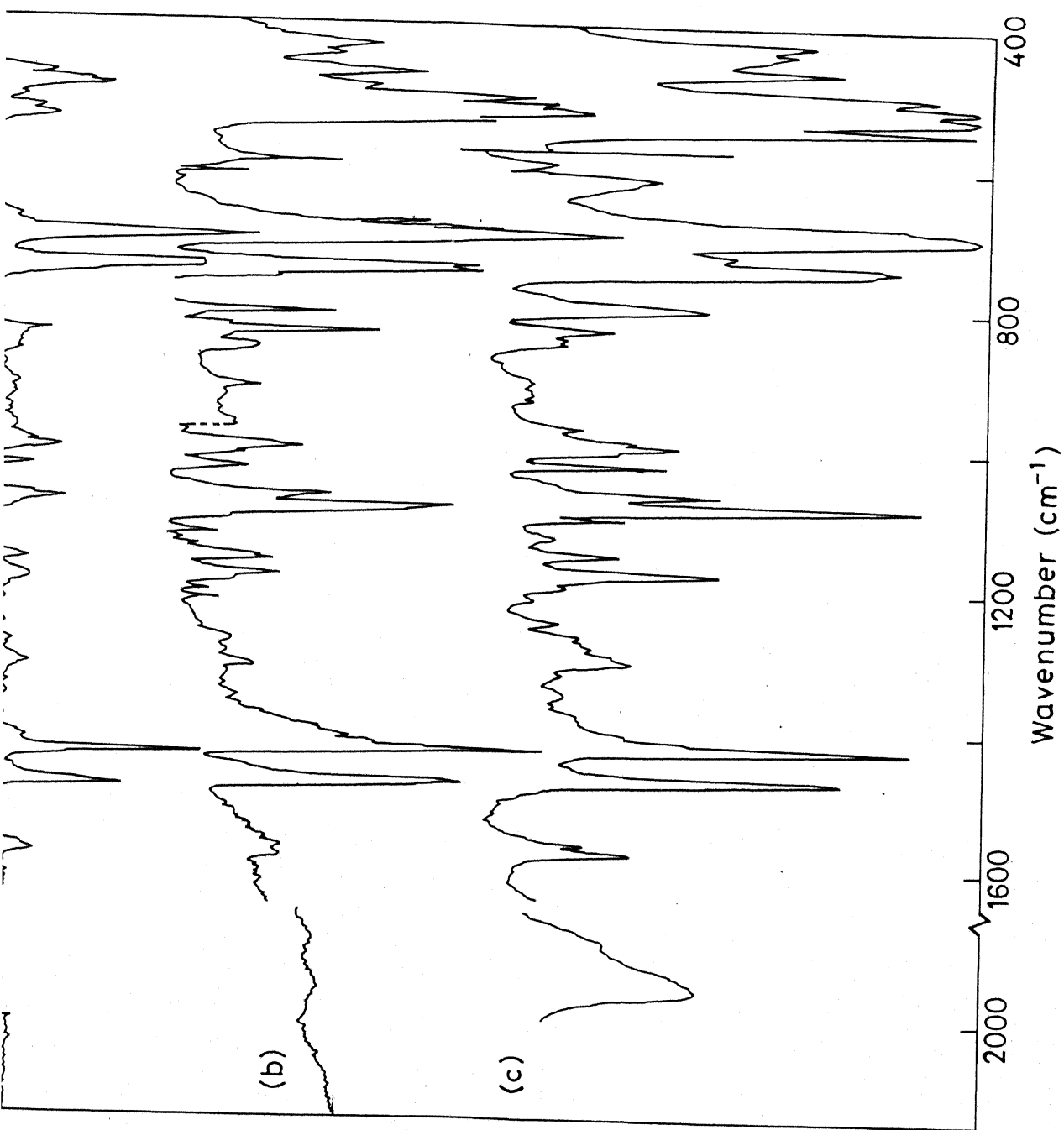


Fig.2B.1 Infrared spectra.



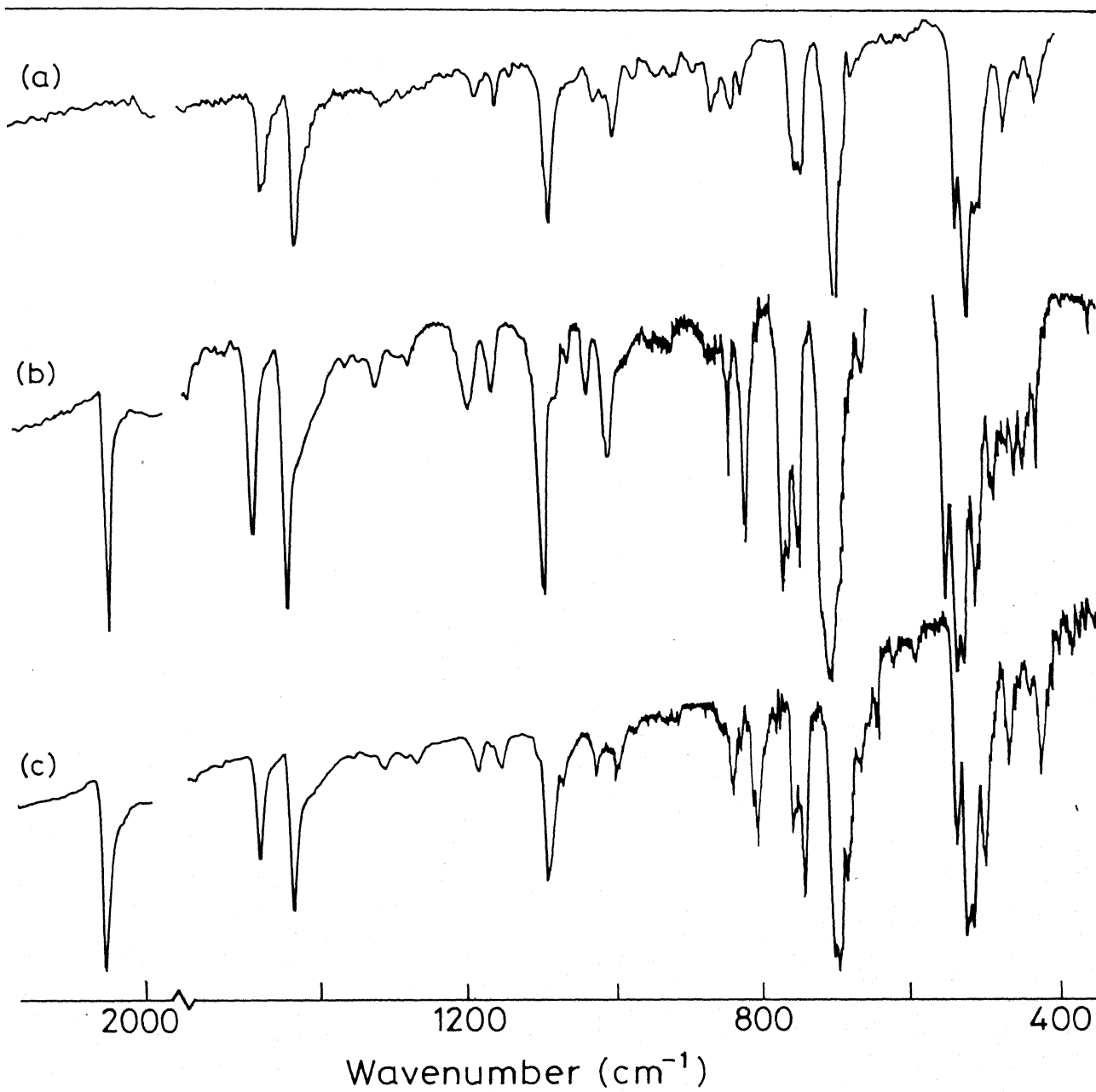
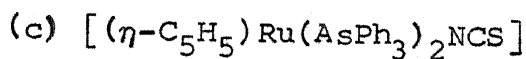
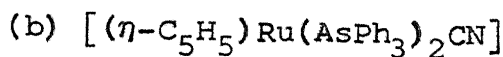
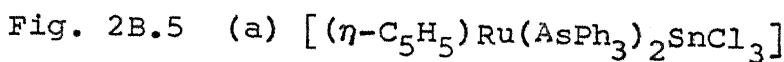
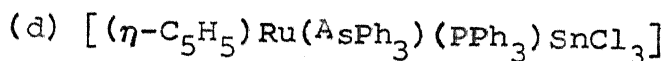
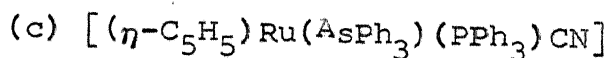
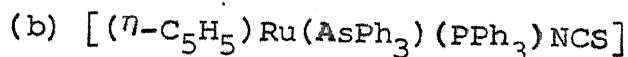
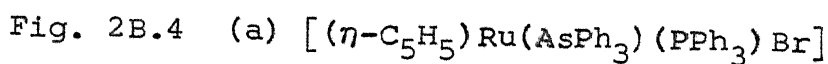
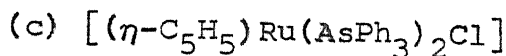
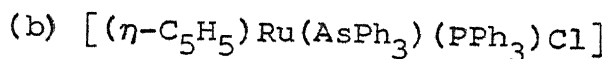
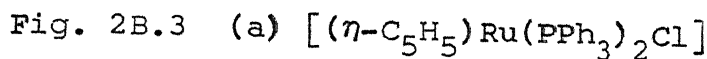


Fig.2B.2 Infrared spectra.

## PROTON NMR SPECTRA OF THE COMPLEXES



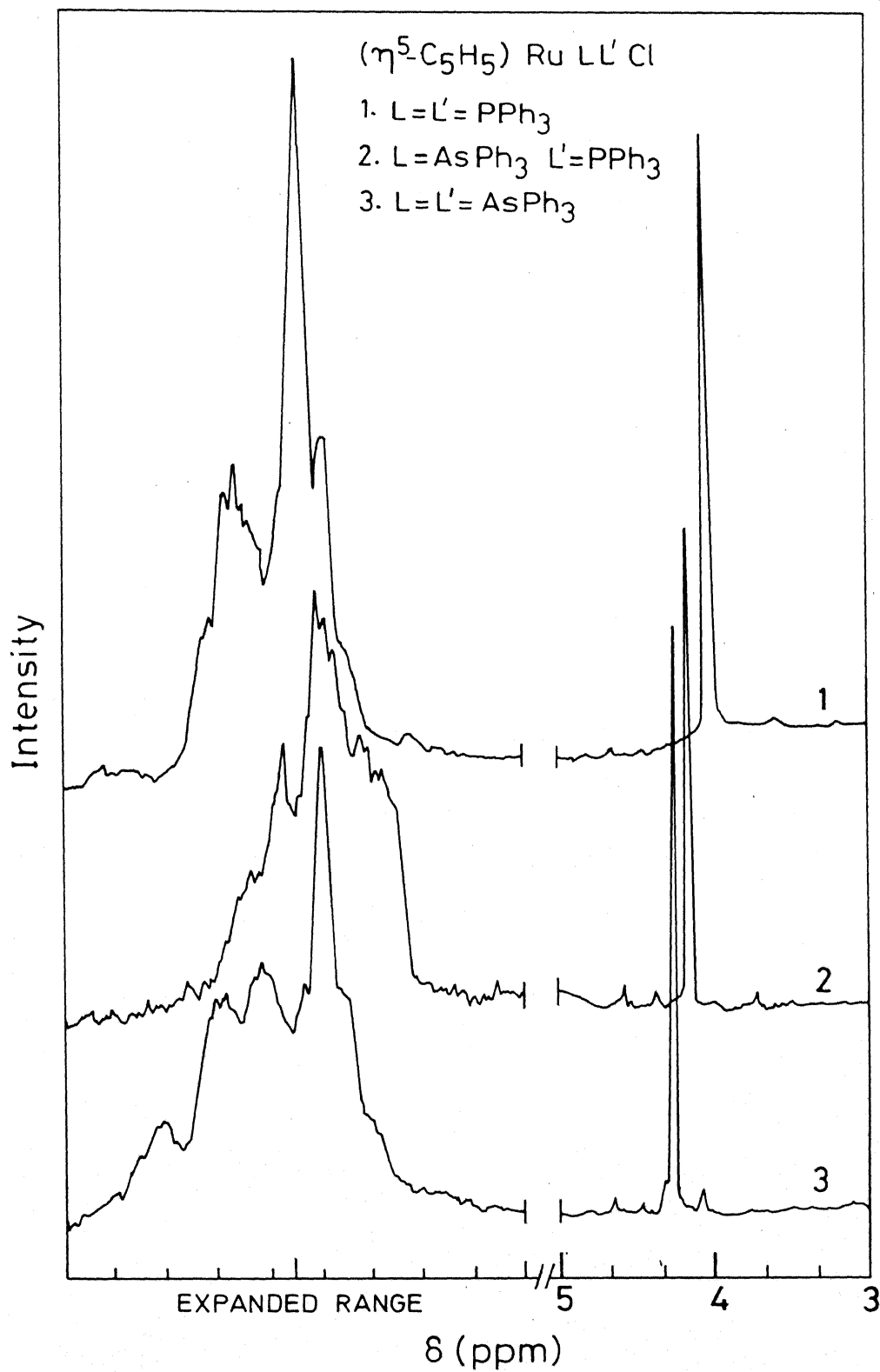


Fig. 2B.3  $^1\text{H}$  NMR spectra of Ru complexes.

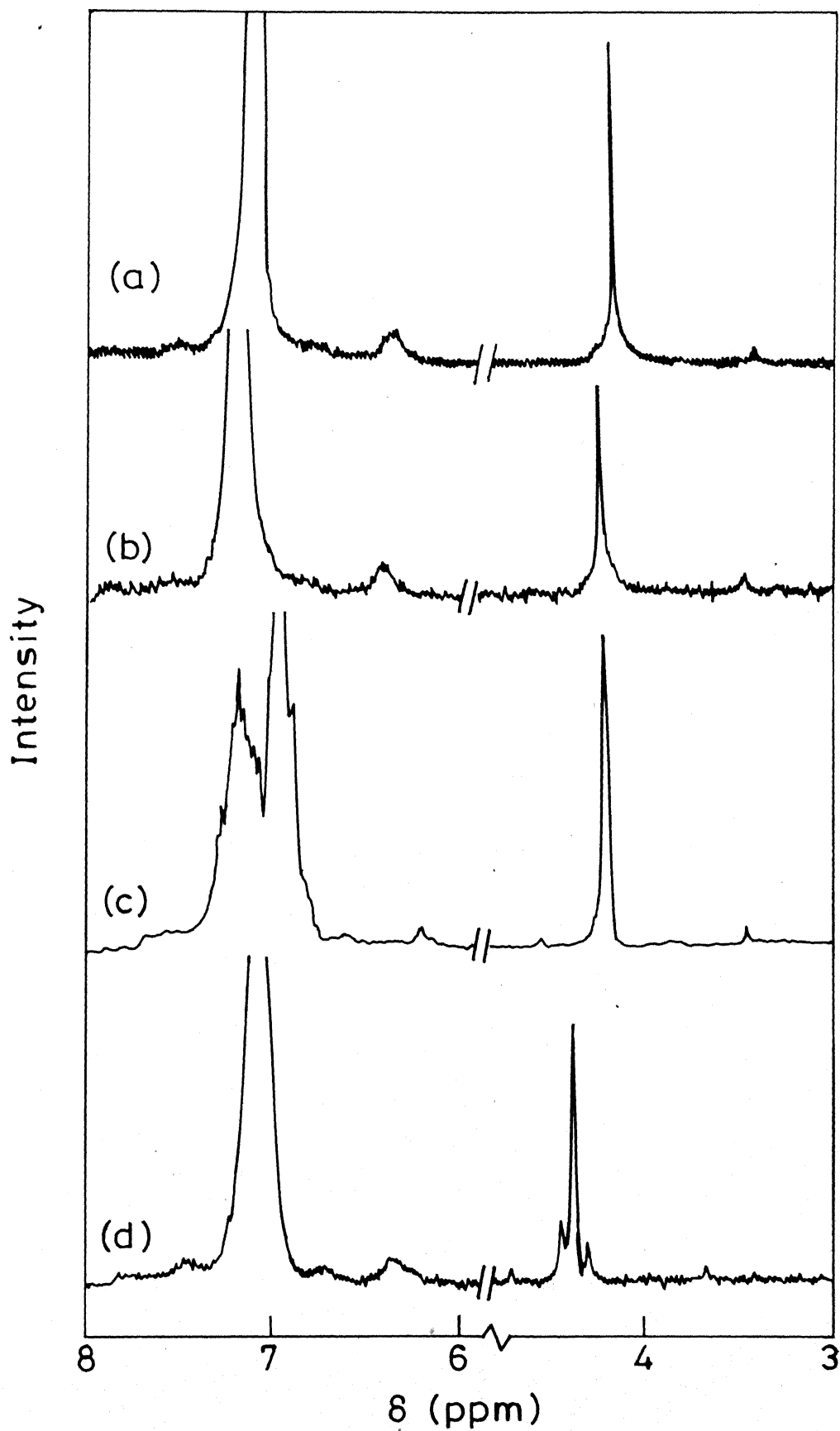


Fig.2B.4  $^1\text{H}$  NMR spectra

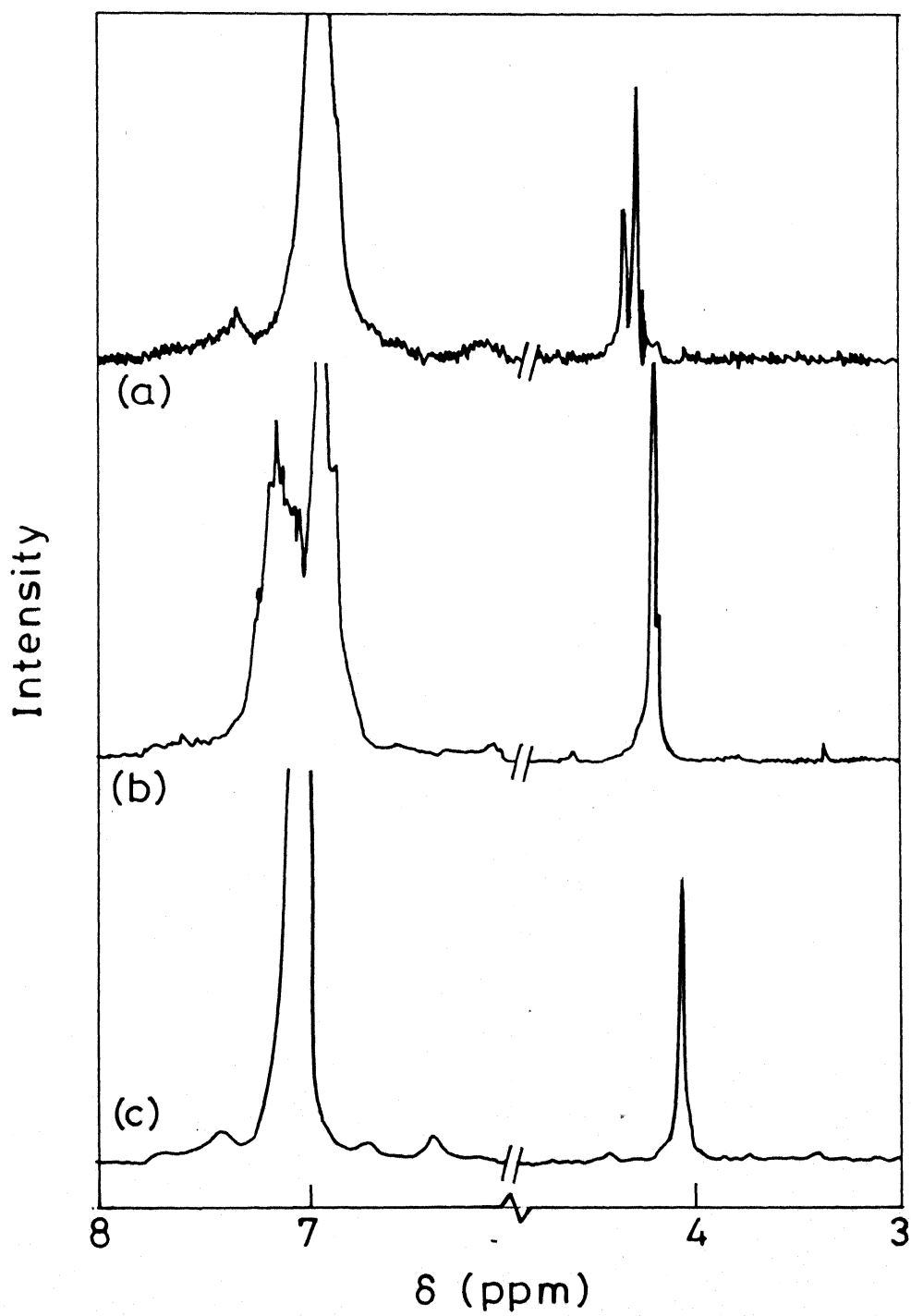


Fig.2B.5  $^1\text{H}$  NMR spectra

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### Chapter III

## BISTRIPHENYLSTIBINE COMPLEXES OF $\eta$ -CYCLOPENTADIENYL-RUTHENIUM(II)

### Introduction

Although recent literature indicates the synthesis and characterization of a number of ruthenium cyclopentadienyl complexes with triphenylphosphine and triphenylarsine as co-ligands<sup>1-5</sup> leading to the formation of neutral as well as cationic complexes, those with triphenylstibine as co-ligand have not been much studied. The chemistry of these might be interesting because of more pronounced steric interaction and the presence of high electron density on ruthenium from two bulky tertiarystibine ligands linked to the metal ion compared to its triphenylphosphine analogues.<sup>6,7</sup> It will, therefore, be worthwhile to study the reactivity of  $\text{SbPh}_3$  with  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{PPh}_3)_2\text{X}]$  ( $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-, \text{SnCl}_3^-, \text{NCS}^-$ ). In this chapter the results of these reactions have been presented. The bonding modes of the various ligands as characterized by the physical studies, have also been discussed herein.



## Experimental

All the chemicals used were either chemically pure or of Analar grade. The solvents were double distilled and dried before use. The complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{Cl}]$  was prepared by the literature method.<sup>2</sup>

All reactions were carried out under the nitrogen atmosphere.

### Preparation of the Complexes

#### (a) Preparation of Monochloromono( $\eta$ -cyclopentadienyl)bis(triphenylstibine) ruthenium(II), $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{Cl}]$ (I)

$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{Cl}]$  (100 mg, 0.12 mmol) and  $\text{SbPh}_3$  (100 mg, ca. 0.28 mmol) were heated under reflux in 20 ml of benzene for 30 hr. The resulting solution was concentrated to about 3 ml and the complex was precipitated with light petroleum as brick-red coloured micro-crystals. The crystalline product was recrystallised from  $\text{CH}_2\text{Cl}_2$ /light petroleum. It was centrifuged, washed with excess of petroleum ether and dried under vacuum. The purity of the compound was checked on TLC and analysed (yield: ca. 90%).

#### b) Preparation of Mono( $\eta$ -cyclopentadienyl)monohydrido-bis(triphenylstibine) ruthenium(II), $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{H}]$ (II)

The complex (I) (100 mg, ca. 0.11 mmol) was taken in 20 ml methanol and sodium metal (5 mg, ca. 0.12 mmol) was added to it.

The resulting mixture was heated under reflux for 20 minutes and the solution was slowly concentrated, whereupon a yellow complex precipitated out. It was centrifuged, washed with methanol and dried under vacuum and analysed for  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{SbPh}_3)_2\text{H}]$  (yield: ca. 67%).

(c) Preparation of Monohalomono( $\eta$ -cyclopentadienyl)bis(tri-phenylstibine)ruthenium(II),  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{X}]$  ( $\text{X} = \text{F}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ )

(i) 100 mg (ca. 0.11 mmol) of the complex (II) was dissolved in 10-15 ml methanol and a few drops of HX was added to it. It was stirred for about 10 min. whereby a microcrystalline precipitate appeared whose colour varied from brick-red to brown-red (depending upon the nature of halide ion). It was centrifuged, washed with water, methanol, ether and light petroleum, dried in vacuum and analysed (yield: ca. 80-90%).

(ii) Monoiodo and monobromo substituted derivatives were also synthesized by heating under reflux for one hr, the complex (I) (100 mg, ca. 0.12 mmol) with a slight excess of KX in ethanol (25 ml), and treating the resulting mixture by the same procedure as described under (i).

(iii) The iododerivative of the complex was prepared by dissolving the complex (II) (100 mg, ca. 0.11 mmol) in methanol (10 ml) and treating the resulting solution with MeI (a few drops, ca. 0.2 ml) whereupon a yellowish orange solution was

immediately formed. After stirring the solution for about 5 min. brownish orange crystals separated which were centrifuged, washed with methanol, ether, light petroleum and dried under vacuum and analysed.

(d) Preparation of  $\eta$ -Cyclopentadienylbis(triphenylstibine)trichlorotinruthenium(II),  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{SnCl}_3]$

A mixture of complex (I) (100 mg, ca. 0.12 mmol) and  $\text{SnCl}_2$  (50 mg, ca. 0.27 mmol) was heated under reflux for 30 min. in a mixture of benzene (15 ml) and methanol (20 ml), whereupon yellow crystals of the complex were separated. These were centrifuged and from the centrifugate, more crystals were obtained by concentrating the solution and subsequent filtration. The complex was recrystallised from  $\text{CH}_2\text{Cl}_2$ /light petroleum. These were dried under vacuum and analysed (yield: ca. 50%).

(e) Preparation of Mono( $\eta$ -cyclopentadienyl)mono(cyano or thiocyanato)bis(triphenylstibine)ruthenium(II),  $[\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{SbPh}_3)_2\text{X}]$  (X = CN or NCS)

A solution of complex (I) (100 mg, ca. 0.12 mmol) and three-fold excess of KCN or KSCN in methanol or ethanol (20 ml) was heated to reflux for five hours in the case of cyano complex and for two hours in that of thiocyanato complex. Concentration of the resulting solution led to the separation of yellowish-green crystals (cyano) or yellow crystals for

thiocyanato complex. These were centrifuged, washed with water, ethanol and light petroleum and dried under vacuum (for cyano, yield: ca. 50% , and thiocyanato complex, yield: ca. 60%) and analysed.

(f) Preparation of the Salts of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2(\text{MeCN})]^+\text{Y}^-$   
( $\text{Y}^- = \text{BPh}_4^-$ ,  $\text{HgCl}_3^-$  and  $\text{Zn}_2\text{Cl}_6^{2-}$ )

(i) Tetraphenylborate salt- Addition of  $\text{NaBPh}_4$  (60 mg, ca. 0.17 mmol) to a solution of complex (I) (100 mg, ca. 0.12 mmol) in acetonitrile (20 ml), followed by heating for a brief period under reflux gave a yellow solution. The resulting solution was filtered and the filtrate was concentrated to half the volume. Addition of ether to the concentrate gave a yellow microcrystalline precipitate which was centrifuged, washed, ethanol, ether and petroleum ether. This was recrystallised from acetonitrile-ether to give the tetraphenylborate salt (yield: ca. 50%).

(ii) Trichloromercury salt- The reaction was carried out by the procedure similar to that described in (i) except that mercury(II) chloride (20 mg, ca. 0.74 mmol) was used in the place of tetraphenylborate to obtain  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2(\text{MeCN})]^- [\text{HgCl}_3]$  (yield: ca. 53%).

(iii) Hexachlorodizincate salt- The reaction was carried out by the procedure similar to that described in (i) except that zinc(II) chloride (20 mg, ca. 0.16 mmol) was used in the place of tetraphenylborate to obtain  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2(\text{MeCN})]_2 [\text{Zn}_2\text{Cl}_6]$

(yield: ca. 55%).

### Physical Measurements

Carbon, hydrogen, nitrogen percentage in the reaction products were analysed by the Microanalytical Section of the Indian Institute of Technology, Kanpur. Halogens and sulfur were analysed by the standard method<sup>8</sup> in the filtrate obtained after fusing the sample with  $\text{KNO}_3$  and  $\text{NaOH}$  and extracting the melt by water and filtering it. IR, UV and Visible, magnetic moments and melting points were determined by the procedure described elsewhere.<sup>1</sup> The positions of the major bands in the IR and electronic spectra of the complex (I) along with other data are given in Table III.1.

The mass spectrum was recorded by a JEOL 01SG-2 mass spectrometer with an ionising energy of 70 eV. X-ray powder diffraction pattern of the complex (I) was recorded with ISO-Debyeflex 2002 diffractometer.

### Results and Discussion

The analytical data of the complex (I) suggested its formula to be  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{Cl}]$  which is formed as a result of substitution reaction of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{Cl}]^2$  by triphenylstibine. It is air stable highly soluble in chloroform,  $\text{CH}_2\text{Cl}_2$ , benzene, partially soluble in ethanol, methanol, diethyl ether, and insoluble in petroleum-ether, n-hexane. This formulation was

further confirmed by the determination of molecular weight by mass spectrometry which gave a molecular ion peak at 908 m/e. Besides the intense molecular ion peak, a large number of other small peaks were also present, amongst them three were a few prominent ones at m/e 829, 828, 727 & 279. The latter ones may be due to the formation of the species as shown in Fig. 3.1 from the parent molecule. These fragments have been postulated on the basis of the appearance of similar fragments in analogous system.<sup>9,10</sup> Besides these, other with masses corresponding to  $\text{SbPh}_3$ ,  $\text{SbPh}_2$ ,  $\text{Ph}$ ,  $\text{C}_5\text{H}_5$  etc. are also present in the spectrum.

The X-ray powder spectra of the complex (I) is found to be identical to that of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  as far as the peak positions are concerned, however, the peak intensity in the two cases were found to be different. It suggests that both the complexes are isomorphous. The structure of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  has already been established previously.<sup>6</sup> We assign the same structure to our stibine complex as that of phosphine analogue.

The complex (I) was further subjected to substitution reaction in order to confirm the above formulation. It has been experimentally observed that all the reactions led to the scission of Ru-Cl bond leading to the formation of the substitution products with other halogens and pseudo halogens like  $\text{F}^-$ ,  $\text{H}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SnCl}_3^-$ ,  $\text{CN}^-$  and  $\text{NCS}^-$ .

Reactions between the chloro complex and zinc or mercury(II) chlorides in acetonitrile produced rapid colour change from

orange to yellow of the solution from which stable yellow complexes were isolated. These were initially believed to be single 1:1 adducts in which the ruthenium complex act as a Lewis base. Further investigation revealed that the products were the salts of the cation  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2(\text{MeCN})]^+$ .

### Magnetic Moments and Electronic Spectra

All the complexes were found to be diamagnetic, indicating spin pairing. In all of them the symmetry of the donor atoms around the metal centre may be considered to be distorted octahedral, based upon the assumption that the cyclopentadienyl group occupying three coordinate sites or distorted tetrahedral if the perpendicular axis of the  $\text{C}_5$  ring is considered to occupy one position, the diamagnetism of the complexes is, however, strongly suggestive of the former alternative, because of the definite possibility of spin free complexes in tetrahedral environment.

The position of the absorption bands noticed in the UV and visible region of the electronic spectra of the complex (I) were at 380 nm and shoulder at 480 nm due to  $(\text{M} \rightarrow \text{L})$  charge transfer band. When we compared complex (I) with  $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}]$  and  $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)_2\text{Cl}]$  complexes the absorption bands showed red shifts. The red shift in the triphenylstibine complex may be due to the weak crystal field of the stibine compared to that of arsine and phosphine.

## Infrared Spectra

IR spectra of all the complexes exhibited two bands of medium intensity in the region  $830\text{--}840\text{ cm}^{-1}$  and  $420\text{ cm}^{-1}$  assigned to out-of-plane bending mode of  $\text{C}_5\text{H}_5$  and the skeletal modes of the ring vibration, respectively. In addition, the characteristic bands of triphenylstibine<sup>11,12</sup> were present in the spectra. In the spectrum of the hydride complex a band at  $1950\text{ cm}^{-1}$  assigned to  $\nu(\text{Ru-H})^5$  appeared and in the case of cyano complexes at  $2100\text{ cm}^{-1}$  and  $2120\text{ cm}^{-1}$ , respectively due to stretching mode of CN.<sup>13</sup>

The salts of the complex cation  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2^-(\text{MeCN})]^+$  can be formed directly by dissolution of (I) in acetonitrile in the presence of tetraphenylborate ion,  $\text{HgCl}_2$  or  $\text{ZnCl}_2$  which yielded yellow crystalline products. IR spectra of these salts exhibited only a very weak band around  $2150\text{ cm}^{-1}$  due to  $\nu(\text{CN})$  of the coordinated acetonitrile.<sup>7</sup> Besides, the spectra also showed extra bands in the region  $400\text{--}200\text{ cm}^{-1}$  characteristic of  $[\text{Zn}_2\text{Cl}_6]^{2-}$  or  $\text{HgCl}_3^-$  anions. The spectrum of  $\text{HgCl}_3^-$  salt exhibited a band at  $285\text{ cm}^{-1}$ , which has been assigned to the asymmetric stretching mode in  $(\text{HgCl}_3)^-$ . This band was not present in the spectrum of  $(\text{Zn}_2\text{Cl}_6)^{2-}$  salt. Instead, four bands at  $330\text{ cm}^{-1}$ ,  $300\text{ cm}^{-1}$ ,  $242\text{ cm}^{-1}$  and  $230\text{ cm}^{-1}$  were present in the spectrum, whose positions and relative intensities are similar to those present in IR spectra of the complexes  $\text{B}^+(\text{ZnCl}_3)^-$  ( $\text{B} = \text{bipy}, \text{BPh}_2^+$ ) where it has shown<sup>14,15</sup> that  $\text{ZnCl}_3^-$  is present in



the dimeric bridge form,  $(\text{Zn}_2\text{Cl}_6)^{2-}$ , rather than the mononuclear  $(\text{ZnCl}_3)^-$  anion. It has, therefore, been suggested that in the  $\text{ZnCl}_3^-$  salt of the ruthenium complex cation,  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2(\text{MeCN})]^+$ ,  $\text{ZnCl}_3^-$  is present as  $(\text{Zn}_2\text{Cl}_6)^{2-}$  species.

### NMR Spectra

$^1\text{H}$  NMR spectra of all the complexes showed a sharp peak around  $\delta 4.2$  and  $\delta 4.3$ . Although it is difficult to assign any definite reason for the presence of three bands in this region, it has, however, been observed that in a few complexes the triphenylphosphine derivative also exhibited triplet around  $\delta 4.55$  due to the coupling of phenyl proton with those of cyclopentadienyl ones.<sup>3,7</sup> Since the presence of three peaks (approx. 1:2:2, some cases 1:3:1) in the expected range of  $[\eta\text{-C}_5\text{H}_5]$  ( $\delta 4.0 - 5.0$ ),<sup>3</sup> it is possible that the five protons of cyclopentadienyl ring are not equivalent which may be caused due to slight tilt of cyclopentadienyl ring towards, one of the triphenylstibine molecule, so that the phenyl proton of  $\text{SbPh}_3$ , interact the cyclopentadienyl proton or hindered rotation of  $\text{Ru-}\eta\text{-C}_5\text{H}_5$  bond, because of bulky  $\text{SbPh}_3$  ligands. When we replaced one of the  $\text{SbPh}_3$  ligand with pyridine, we observed single sharp peak due to cyclopentadienyl protons.<sup>16</sup> However, it is only a tentative explanation. In the case of acetonitrile

cationic complexes an additional signal due to the methyl protons was observed in the region  $\delta$  1.8 to  $\delta$  2.0. The aromatic protons of the triphenylstibine showed characteristic bands in the range of  $\delta$  7.0-8.0 ppm.

Table III.1. Characterization Data

Complex (M.Wt.)	M.P. (°C)	Colour <sup>a</sup>	Analysis, Found (Calcd.), %				IR bands		<sup>1</sup> H NMR (δ ppm)
			C	H	N	X/S	(cm <sup>-1</sup> ) (C <sub>5</sub> H <sub>5</sub> )	(C <sub>5</sub> H <sub>5</sub> )	
1	2	3	4	5	6	7	8	9	
[(η-C <sub>5</sub> H <sub>5</sub> )Ru(SOPh <sub>3</sub> ) <sub>2</sub> Cl] (908)	153-5	BR	54.4 (54.2)	4.2 (3.9)	-	4.5 (3.9)	830		4.16
[(η-C <sub>5</sub> H <sub>5</sub> )Ru(SbPh <sub>3</sub> ) <sub>2</sub> H] (873)	135 <sup>d</sup>	Y	56.5 (56.3)	4.5 (4.1)	-	-	840, 1950 ν(Ru-H)		4.15
[(η-C <sub>5</sub> H <sub>5</sub> )Ru(SOPh <sub>3</sub> ) <sub>2</sub> F] (891)	145-7	BR	54.7 (55.2)	4.2 (3.9)	-	-	830, 500, 480 <sup>c</sup> , ν(Ru-F)		4.16
[(η-C <sub>5</sub> H <sub>5</sub> )Ru(SOPh <sub>3</sub> ) <sub>2</sub> Br] (952)	148	B	52.1 (51.7)	4.1 (3.7)	-	9.2 (8.4)	840		4.16
[(η-C <sub>5</sub> H <sub>5</sub> )Ru(SbPh <sub>3</sub> ) <sub>2</sub> I] (999)	150	BO	49.5 (49.2)	4.0 (3.3)	-	13.2 (12.7)	840		4.18
[(η-C <sub>5</sub> H <sub>5</sub> )Ru(SbPh <sub>3</sub> ) <sub>2</sub> SnCl <sub>3</sub> ] (1097)	210	OY	44.2 (44.8)	3.5 (3.2)	-	10.2 (9.7)	840		4.10
[(η-C <sub>5</sub> H <sub>5</sub> )Ru(SbPh <sub>3</sub> ) <sub>2</sub> CN] (898)	245	YG	55.9 (56.1)	4.2 (3.9)	1.5 (1.6)	-	840, 2100 ν(CN)		4.50
[(η-C <sub>5</sub> H <sub>5</sub> )Ru(SOPh <sub>3</sub> ) <sub>2</sub> NCS] (930)	135	Y	54.4 (54.2)	4.1 (2.8)	1.5 (1.5)	4.0 (3.4)	850, 2120 ν(CN)		4.30

.....contd.

Table III.1 (contd.)

1	2	3	4	5	6	7	8	9
$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SOPh}_3)_2(\text{MeCN})]\text{BPh}_4$ (1232)	148-50	OY	64.8 (65.2)	5.1 (4.7)	1.3 (1.1)	-	850	-
$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SOPh}_3)_2(\text{MeCN})]\text{HgCl}_3$ (1220)	152-5	OY	42.5 (42.3)	3.5 (3.1)	1.5 (1.4)	8.5 (8.7)	850	4.0 in $\text{CH}_2\text{Cl}_2$
$[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SOPh}_3)_2(\text{MeCN})]_2\text{-Zn}_2\text{Cl}_6$ (2170)	190-5	OY	47.5 (47.6)	3.7 (3.5)	1.4 (1.3)	10.2 (9.8)	850	-

<sup>a</sup> BR = brick-red, Y = yellow, B = brown, BO = brownish orange, OY = orange-yellow, YG = yellowish green.

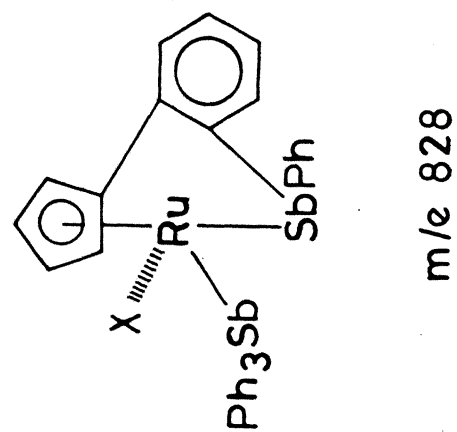
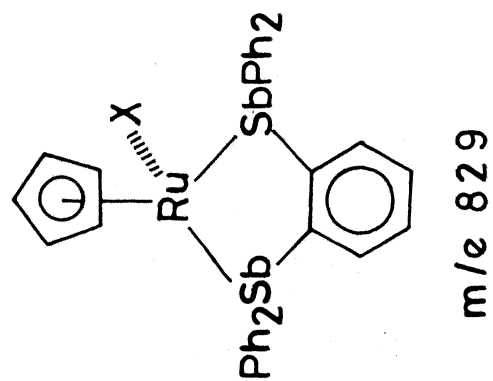
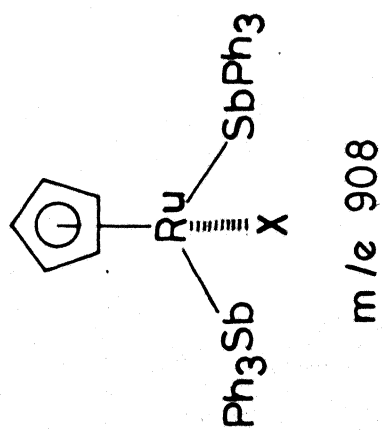
<sup>b</sup> Solvent  $\text{CDCl}_3$ , Aromatic protons of the other coligands appeared in the region  $\delta$  7-8 as broad multiplets, and in the case of acetonitrile complex additional signals in the region  $\delta$  1.8-2.0 were observed due to the methyl protons.

<sup>c</sup> Metal-Ligand and related vibrations, D.M. Adams, New York, St. Martins Press (1968).

Fig. 3.1 The proposed structures for molecular ions observed in the mass spectrum of complex I.

#### IR SPECTRA OF THE COMPLEXES

- Fig. 3.2
- (a)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{F}]$
  - (b)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{CN}]$
  - (c)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{Cl}]$
  - (d)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{H}]$
  - (e)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{NCS}]$
  - (f)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{SnCl}_3]$



$\text{X} = \text{Cl}$

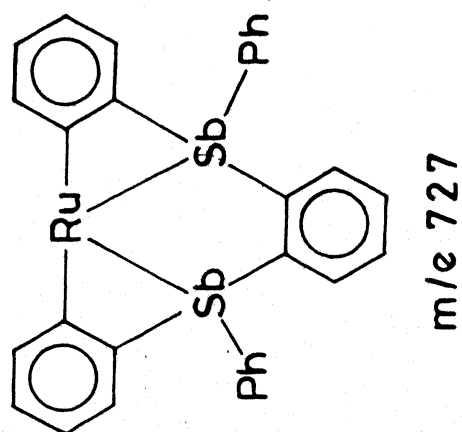
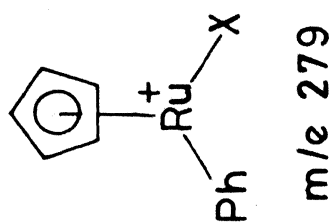


FIG. 3.1

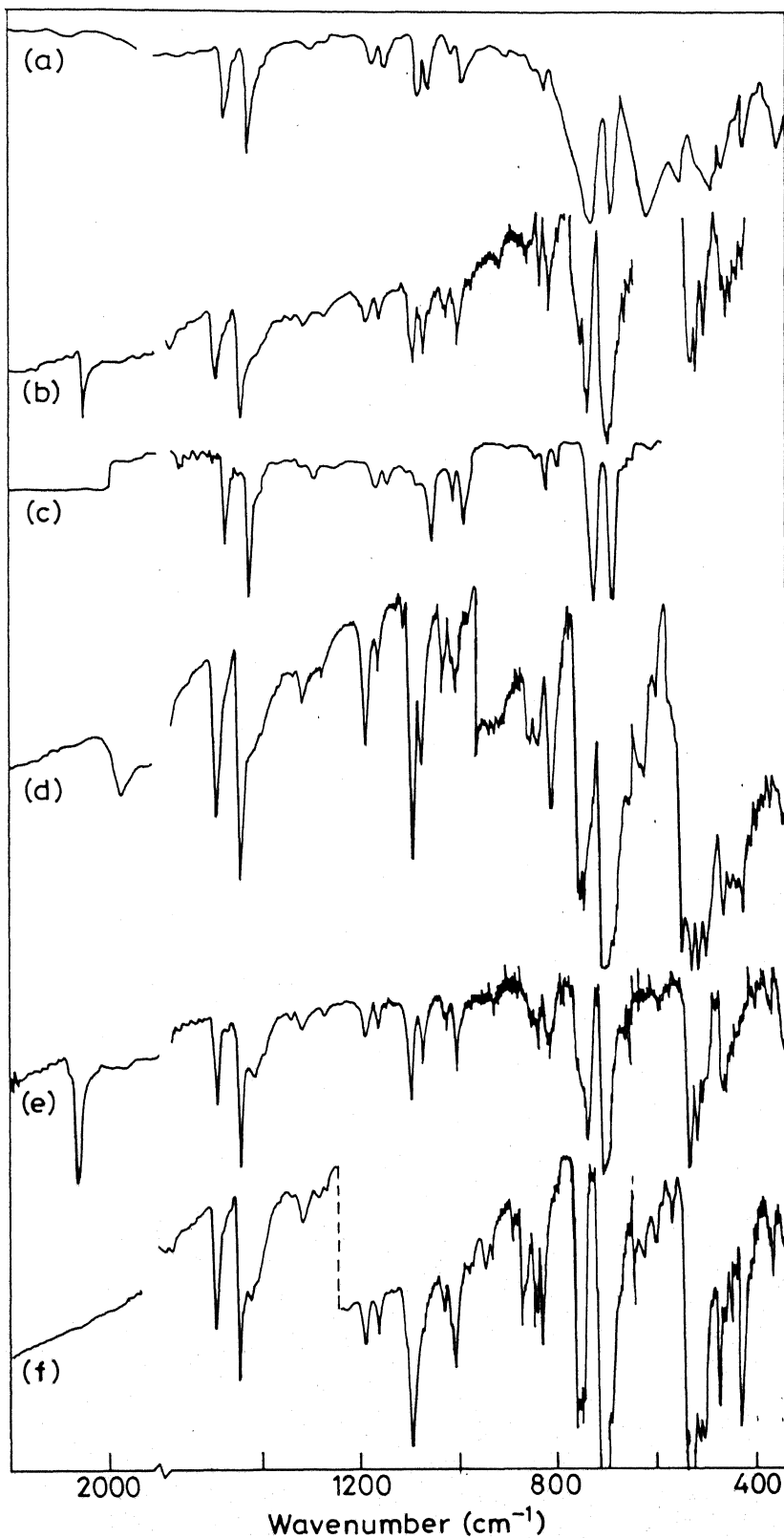
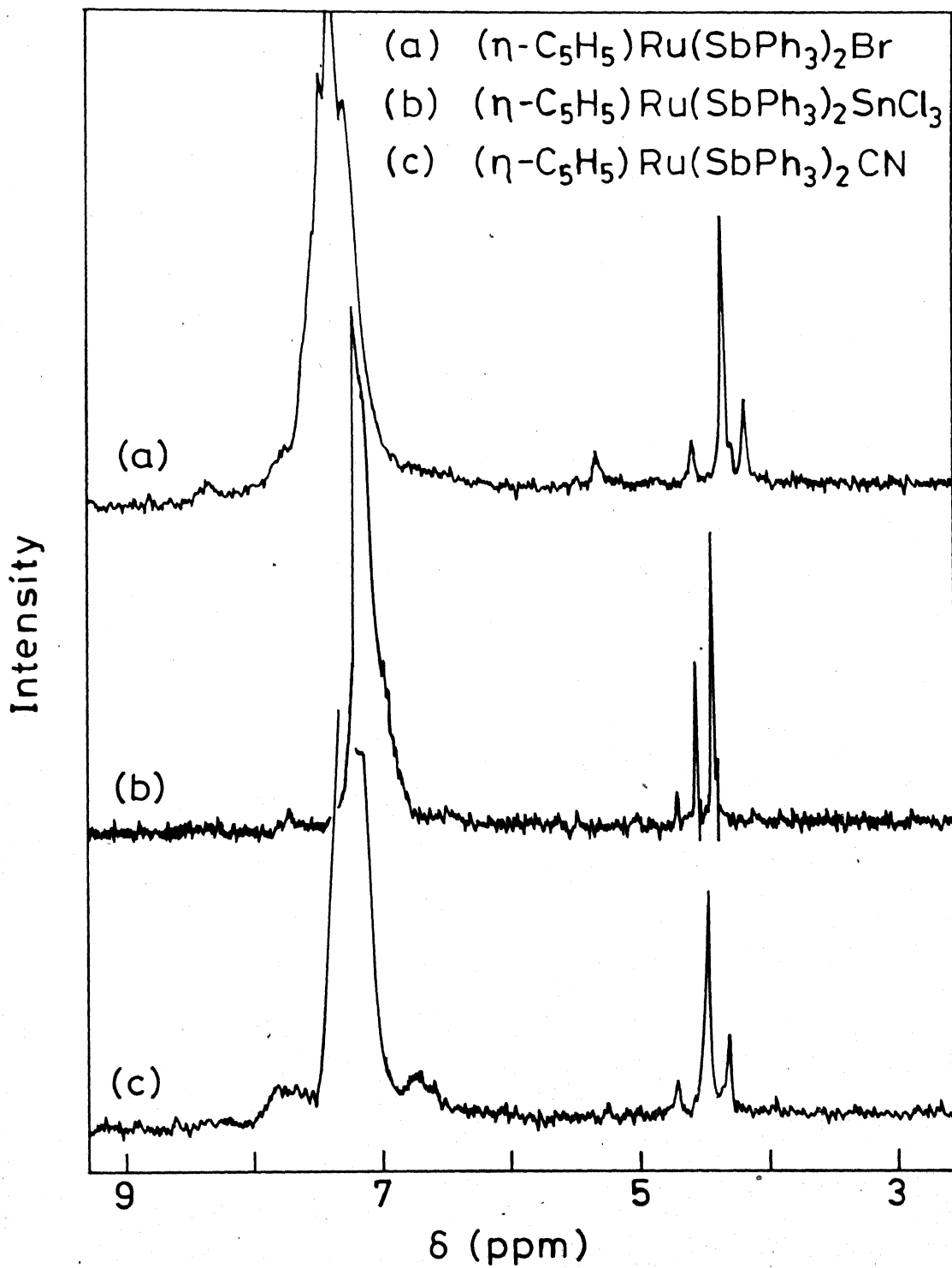


Fig.3.2 Infrared spectra.

Fig. 3.3  $^1\text{H}$  NMR spectra



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## Chapter IV

### SUBSTITUTION REACTION OF $\eta$ -CYCLOPENTADIENYL RUTHENIUM(II) COMPLEXES WITH NITROGEN, OXYGEN AND SULFUR DONOR LIGANDS

#### Introduction

The unusual chemistry of cyclopentadienyl ruthenium complexes,  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{ER}_3)_2\text{X}]$  ( $\text{E} = \text{P, As, Sb; R} = \text{Ph, Me, OPh}$ ) has captured the attention of many investigators for the past several years.<sup>1-12</sup> In continuation of our previous work<sup>10</sup> we wished to examine the reactions of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$  ( $\text{E} = \text{As or Sb}$ ) and  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{X}]$  ( $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-, \text{NCS}^-$  and  $\text{SnCl}_3^-$ ) towards heterocyclic bases like pyridine,  $\gamma$ -picoline, 2,2'-bipyridine, 1,10-phenanthroline and towards sodium diethyldithiocarbamate and acetylacetone. This chapter reports the results of such a study.

#### Experimental

All the chemicals used were chemically pure or Analar grade. Solvents were distilled and dried before use. The complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{PPh}_3)\text{X}]$  and  $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{EPh}_3)_2\text{X}]$

(E = As or Sb; X =  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{NCS}^-$  and  $\text{SnCl}_3^-$ ) were prepared by the literature procedures.<sup>11,12</sup>

### Typical Methods of Synthesizing the Complexes

(a) Preparation of the Complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)\text{LX}]$  (E = As, Sb; L = Py,  $\gamma$ -pic) and  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)\text{L-L}]^+\text{X}^-$  (E = P, As, Sb; X =  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{NCS}^-$ ,  $\text{SnCl}_3^-$ ,  $(\text{DTC})^-$  and  $(\text{acac})^-$ )

The complexes were synthesized by refluxing  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$  (ca. 0.12 mmol) in 20 ml ethanol with the corresponding substrate for several hours. After concentrating the resulting solution to nearly 5 ml<sup>†</sup> a slight excess of diethyl ether (ca. 20 ml) was added yielding a microcrystalline product. It was separated by centrifugation and recrystallized from the appropriate solvent. The recrystallized product was washed with light petroleum, and air dried.

Attempts to synthesize the corresponding arsine complexes having diethyldithiocarbamate or acetylacetonate as coligands were unsuccessful.

(b) Preparation of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)\text{L-L}]^+\text{Y}^-$  (E = As or Sb;  $\text{Y}^- = \text{BPh}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ ,  $\text{HgCl}_3^-$  and  $\text{Zn}_2\text{Cl}_6^{2-}$ )

These were synthesized by metathesis reactions. The complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)\text{L-L}]^+\text{X}^-$  (ca. 0.1 mmol) in 15 ml of

<sup>†</sup> The solution was concentrated to get a better yield of the complex. It also appeared without concentration, but the yield was poor.

ethanol on mixing with equimolar quantity of  $Y^-$  in ethanol (5 ml) yielded an immediate orange red precipitate. (Perchlorates of these cations could also be isolated by the addition of a few drops of perchloric acid to their alcoholic solutions, but one should be careful in their syntheses because of their high explosive nature.) The precipitated residue was separated by filtration, washed with diethyl ether and recrystallized by chloroform/methanol mixture.

Using ethanol as solvent no stable product was obtained by the reaction of bipyridine or 1,10-phenanthroline with  $[(\eta-C_5H_5)Ru(EPh_3)_2H]$  ( $E = As$  or  $Sb$ ). However, in the presence of anions  $BPh_4^-$ ,  $BF_4^-$ ,  $ClO_4^-$ ,  $HgCl_3^-$  and  $Zn_2Cl_6^{2-}$  the same reaction mixture yielded the stable cationic salts  $[(\eta-C_5H_5)Ru(EPh_3)-(L-L)]^+$  ( $E = As$  or  $Sb$ ;  $L-L = 2,2'$ -bipy, 1,10-phen). The same reactions carried out in halohydrocarbons such as  $CH_2Cl_2$ ,  $CHX_3$  etc. gave the corresponding halide salts  $[(\eta-C_5H_5)Ru(EPh_3)-(L-L)]^+X^-$  ( $X = Cl, Br$ ) which in the presence of a large anion,  $Y^-$  afforded the corresponding salt of  $Y^-$ .

### Physical Measurements

Carbon, hydrogen and nitrogen analyses were carried out by the Microanalytical laboratory of the Indian Institute of Technology, Kanpur, India. The percentages of halides and sulfur in the complexes were determined by the standard methods<sup>13</sup> in the filtrate obtained after fusing the sample with the fusion

mixture ( $\text{NaNO}_3:\text{NaOH}$ , 1:8), extracting it with distilled water and filtering it. IR, UV and visible,  $^1\text{H}$  NMR spectroscopic and magnetic measurements were carried out by the methods described elsewhere.<sup>10,11</sup> The results are given in Table IV.1.

The specific reaction conditions, the analytical data, and other physical properties are given in Table IV.1.

### Results and Discussion

The empirical formulae of the complexes formed by the substitution reactions of N-heterocyclic bases,  $\text{Na}(\text{C}_2\text{H}_5)_2\text{NCS}_2$ , or acetylacetone with the complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$  ( $\text{E} = \text{As/Sb}$ ;  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{NCS}^-$  and  $\text{SnCl}_3^-$ ) are listed in Table IV.1. These are air-stable, highly soluble in organic polar solvents like  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , etc. and relatively less soluble in methanol and ethanol.

The formation of identical substitution product from both  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{X}]$  with heterocyclic bases is not surprising, because of the substitution of a larger molecule ( $\text{PPh}_3$ , cone angle  $145^\circ$ ) in the latter by a smaller one ( $\text{AsPh}_3$  cone angle)<sup>14</sup> due to steric hindrance.

An interesting aspect of these reactions is the formation of the cationic complexes with 2,2'-bipyridine and 1,10-phenanthroline while pyridine and  $\gamma$ -picoline gave neutral ones. Under our reaction conditions we were not able to isolate the cationic complexes with pyridine or  $\gamma$ -picoline similar to those reported

by Uson, et al.<sup>15</sup> Although one could have anticipated the formation of cationic complexes  $[(\eta\text{-C}_5\text{H}_5)\text{RuL}_2(\text{EPh}_3)]^+\text{X}^-$  (E = As, Sb; L = Py,  $\gamma$ -pic) in the case of pyridine and  $\gamma$ -picoline also. Seemingly the chelate effect of the ligands, L-L, plays a significant role in stabilizing the cationic complexes. The cationic nature of the complexes has been confirmed: (a) by exchange reactions using cationic and anionic exchangers (Dowex 50W-XB and Dowex 1-XB) and (b) by synthesizing various salts of the cations with a number of large anions (Table IV.1). It has been shown here that the bipy and 1,10-phen complexes are cationic  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)(\text{L-L})]^+$  (E = As or Sb). Although it was previously reported<sup>10</sup> that the corresponding  $\text{PPh}_3$  complexes have the formula  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{L-L})_{0.5}\text{X}]$ , it was later shown that even the  $\text{PPh}_3$  complexes gave  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{L-L})]^+$  on prolonged refluxing (24 hr) while refluxing for a shorter time a mixture of the latter with the starting material was obtained.

The complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)(\text{L-L})]^+\text{Cl}^-$  (E = As or Sb) were converted to  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)(\text{L-L})]^+\text{X}^-$  ( $\text{X}^- = \text{Br}^-, \text{I}^-, \text{NCS}^-, \text{CN}^-$  and  $\text{SnCl}_3^-$ ) by refluxing in methanol with a molar excess of KBr, KI, KCN, KNCS and  $\text{SnCl}_2$ , respectively with the intermediate  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)(\text{MeOH})(\text{L-L})]^+$  probably formed during these reactions.<sup>16</sup>

The IR spectra of all the complexes exhibited sharp bands of medium intensity in the region  $840\text{-}850\text{ cm}^{-1}$  and

relatively broader bands at  $420\text{ cm}^{-1}$ . These bands have been assigned to the out-of-plane bending and skeletal modes of the  $\text{C}_5\text{H}_5$  ring, respectively. In addition to these, the characteristic bands of triphenylarsine and triphenylstibine ( $530\text{s}$ ,  $1100\text{s}$ ,  $1440$ ,  $1490\text{ cm}^{-1}$ ) together with those of the heterocyclic bases (pyridine ( $1590$ ,  $735\text{ cm}^{-1}$ );  $\gamma$ -picoline ( $1600$ ,  $1505$ ,  $720\text{--}730\text{ cm}^{-1}$ ); 2,2'-bipyridine ( $720\text{--}740$ ,  $840$ ,  $1430\text{--}1435$ ,  $1600\text{--}1590\text{ cm}^{-1}$ )) were also observed.<sup>17-20</sup> Further, in all the spectra, the characteristic pattern of three bands of decreasing intensity lying in the  $540\text{--}500\text{ cm}^{-1}$  region suggested the presence of only one coordinated triphenylarsine or triphenylstibine analogue.<sup>15</sup>

The presence of medium intensity bands due to  $\nu(\text{CS})$  around  $1000\text{ cm}^{-1}$  in the spectra of the dithiocarbamate complexes,<sup>5</sup> and broad and intense bands around  $1600\text{ cm}^{-1}$ , assigned to the mixed vibration having contributions from  $\nu(\text{C=O})$  and  $\nu(\text{C=C})$  in the acetylacetone (acac) complexes<sup>21</sup> suggested the presence of the respective ligands in their complexes.

The cyanide and thiocyanato complexes showed absorption bands at  $2050$  and  $2100\text{ cm}^{-1}$ , respectively indicating the presence of CN and NCS group.<sup>22-24</sup> The spectra of the cationic complexes having  $\text{BF}_4^-$  ( $1050\text{ cm}^{-1}$ ),  $\text{BPh}_4^-$  ( $1100\text{ cm}^{-1}$ ),  $\text{ClO}_4^-$  ( $1100\text{ cm}^{-1}$ ),  $\text{HgCl}_3^-$  ( $292\text{ cm}^{-1}$ ) and  $\text{Zn}_2\text{Cl}_6^{2-}$  ( $335$ ,  $300\text{ cm}^{-1}$ ) exhibited the characteristic bands of the anions.<sup>2,7</sup> The zinc complex showed no bands attributable to the  $\nu(\text{ZnCl})$  of  $\text{ZnCl}_3^-$ .<sup>2</sup>

## $^1\text{H}$ NMR Spectra

$^1\text{H}$  NMR spectra of all the complexes showed sharp resonances in the region  $\delta$  4.4-5.0. In the spectra of the cationic stibine complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)(\text{L-L})]^+\text{X}^-$  ( $\text{L-L} = \text{bipy}, 1,10\text{-phen}$ ) three resonances (1:2:2) were observed whereas for the  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{SbPh}_3)(\text{L})\text{X}]$  ( $\text{L} = \text{Py}$  or  $\gamma\text{-pic}$ ) complexes a sharp singlet was observed. The aromatic protons of the triphenylarsine, triphenylstibine and of the N-donor ligands exhibited broad resonances in the range  $\delta$  7.0-8.5. The complexes having  $\gamma$ -picoline also showed a resonance due to methyl protons around  $\delta$  1.8-2.0. Diethyldithiocarbamate and acetylacetonate containing complexes exhibited additional signals in the region  $\delta$  3.5 ( $\text{CH}_2$ ),  $\delta$  2.0 (methyl) and in the region  $\delta$  5.7 ( $-\text{CH}$ ),  $\delta$  2.23 (methyl), respectively.<sup>5,20</sup> The interesting aspect of these spectra is that the  $\text{C}_5\text{H}_5$  proton resonances in the complexes having bases as coligands were shifted downfield compared to their parent species ( $\delta$  4.2), viz.,  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$  ( $\text{E} = \text{As}$  or  $\text{Sb}$ ). Furthermore, the downfield shift is larger in the cationic species in conformity with those previously observed for other  $\text{Ru-}\eta\text{-C}_5\text{H}_5$  cationic complexes.<sup>1-10</sup>

The downfield shift in the position of  $\text{C}_5\text{H}_5$  protons in all the complexes (neutral or cationic) compared to that in the spectra of the complexes having two molecules of  $\text{EPh}_3$  linked to the ruthenium could possibly be due to the difference in the  $\pi$ -accepting behaviour of the heterocyclic bases and the



triphenylarsine or triphenylstibine.<sup>25</sup>

### Electronic Spectra

The electronic spectra of the complexes showed a fairly intense band around 450 nm, which could be assigned to a metal to ligand charge-transfer ( $M \rightarrow L$ ) transition.<sup>26,27</sup> The variation in the position of the ( $M \rightarrow L$ ) charge-transfer bands with the nature of the heterocyclic bases was not regular.

On the basis of the results discussed in the preceding paragraphs and on the basis of the previous studies<sup>1-12</sup> a distorted octahedral structure has been assigned to all the complexes (Fig. 4.1).

Table IV.1

Special conditions for the synthesis of the complexes and their characterization data

Sl. no.	Complex M.P. ( $^{\circ}\text{C}$ ); Color <sup>b</sup> ; Yield (%)	Reaction conditions <sup>†</sup> (A/B; S (mg); T (h); R'; other conditions)	Analyses: Found (Calcd), %					IR bands $\text{C}_5\text{H}_5$ ( $\text{cm}^{-1}$ )	$\text{C}_5\text{H}_5$ $^1\text{H NMR}$ ( $\delta$ ppm)
			C	H	N	Halide/ Sulfur			
1	2	3	4	5	6	7	8	9	
1.	$[(\text{Cp})\text{Ru}(\text{PPh}_3)(\text{Bipy})]^+\text{I}^-$ (240, O, 60)	A; Bipy (50), 14, EtOH, diethyl ether	55.4 (55.7)	4.5 (3.9)	3.7 (3.9)	18.5 (17.86)	835		4.6
2.	$[(\text{Cp})\text{Ru}(\text{PPh}_3)(\text{o-phen})]^+\text{I}^-$ (245, OR, 60)	A; o-phen (50), 14, EtOH-ether	56.9 (57.1)	3.3 (3.8)	3.5 (3.8)	17.7 (17.3)	830		4.6
3.	$[(\text{Cp})\text{Ru}(\text{PPh}_3)(\text{Bipy})]^+\text{CN}^-$ (250, OY, 60)	A; Bipy (50), 20, $\text{CH}_2\text{Cl}_2$ - light petroleum	66.5 (66.9)	4.2 (4.6)	7.1 (6.9)	-	850 $\nu_{\text{CN}}$ 2080		4.35
4.	$[(\text{Cp})\text{Ru}(\text{PPh}_3)(\text{o-phen})]^+\text{CN}^-$ (265, OY, 65)	A; o-phen (50), 20, $\text{CH}_2\text{Cl}_2$ - light petroleum	67.8 (68.1)	4.7 (4.1)	6.3 (6.6)	-	850 $\nu_{\text{CN}}$ 2055		4.25
5.	$[(\text{Cp})\text{Ru}(\text{PPh}_3)(\text{Bipy})]^+\text{NCS}^-$ (193, OY, 70)	A; Bipy (60), 20, $\text{CHCl}_3$ - light petroleum	63.1 (63.5)	4.9 (4.4)	6.2 (6.5)	5.7 (5.0)	832 $\nu_{\text{CN}}$ 2050		4.4
6.	$[(\text{Cp})\text{Ru}(\text{PPh}_3)(\text{o-phen})]^+\text{NCS}^-$ (203, OY, 70)	A; o-phen (55), 20, $\text{CHCl}_3$ - light petroleum	64.3 (64.9)	4.5 (4.2)	6.1 (6.3)	5.5 (4.8)	832 $\nu_{\text{CN}}$ 2040		4.4
7.	$[(\text{Cp})\text{Ru}(\text{PPh}_3)(\text{Bipy})]^+\text{SnCl}_3^-$ (210, O, 50)	A; Bipy (60), 24, $\text{CHCl}_3$ - light petroleum	48.5 (48.7)	3.7 (3.5)	3.3 (3.5)	13.6 (13.1)	852		4.5
8.	$[(\text{Cp})\text{Ru}(\text{PPh}_3)(\text{o-phen})]^+\text{SnCl}_3^-$ (206, O, 55)	A; o-phen (60), 24, $\text{CHCl}_3$ - light petroleum	50.1 (50.3)	3.9 (3.4)	3.2 (3.4)	13.5 (12.7)	850		4.55

Table IV.1 (contd.)

1	2	3	4	5	6	7	8	9
9.	$[(\text{Cp})\text{Ru}(\text{AsPh}_3)(\text{py})\text{Cl}]$ (106d, Y, 50)	A; Py (0.5-1 ml), 10, evaporation under reduced pressure, $\text{CH}_2\text{Cl}_2$ -light petroleum	57.0 (57.4)	4.0 (4.2)	2.3 (2.4)	6.5 (6.0)	850	4.
10.	$[(\text{Cp})\text{Ru}(\text{AsPh}_3)(\gamma\text{-pic})\text{Cl}]$ (130d, Y, 50)	A; $\gamma$ -pic (0.5-1 ml), 10 $\text{CH}_2\text{Cl}_2$ -light petroleum evaporated under reduced pressure	58.4 (58.0)	4.7 (4.5)	2.2 (2.3)	6.6 (5.8)	840	4.
11.	$[(\text{Cp})\text{Ru}(\text{AsPh}_3)(\text{bipy})]^+\text{Cl}^-$ (230, OY, 70)	A; Bipy (50), 13, EtOH-ether	59.2 (59.7)	4.5 (4.2)	4.0 (4.2)	5.6 (5.3)	845	4.6
12.	$[(\text{Cp})\text{Ru}(\text{AsPh}_3)(\text{o-phen})]^+\text{Cl}^-$ (235, OY, 75)	A; o-phen (70), 13, EtOH-ether	61.6 (61.1)	3.9 (4.1)	4.0 (4.2)	5.5 (5.1)	847	4.7
13.	$[(\text{Cp})\text{Ru}(\text{AsPh}_3)(\text{py})\text{Br}]$ (108, Y, 50)	A; Py (1 ml), 10, evaporation under reduced pressure, $\text{CH}_2\text{Cl}_2$ -light petroleum	53.1 (53.3)	3.5 (4.0)	2.1 (2.2)	13.2 (12.7)	840	4.5
14.	$[(\text{Cp})\text{Ru}(\text{AsPh}_3)(\gamma\text{-pic})\text{Br}]$ (136d, Y, 50)	A; $\gamma$ -pic (1 ml), 11, evaporation under reduced pressure, $\text{CH}_2\text{Cl}_2$ -light petroleum	54.3 (54.0)	4.1 (4.3)	2.0 (3.2)	12.8 (12.4)	840	4.5
15.	$[(\text{Cp})\text{Ru}(\text{AsPh}_3)(\text{bipy})]^+\text{Br}^-$ (250, OY, 65)	A, Bipy (50), 15, EtOH-ether	55.5 (55.9)	4.2 (4.0)	4.1 (4.0)	11.7 (11.3)	845	4.63

Table IV.1 (contd.)

1	2	3	4	5	6	7	8	9
16.	$[(Cp)Ru(AsPh_3)(o\text{-phen})]^+ Br^-$ (250, Y, 70)	A; o-phen (50), 15, EtOH- ether	57.0 (57.4)	3.5 (3.8)	4.0 (3.8)	11.3 (10.9)	850	5.0
17.	$[(Cp)Ru(AsPh_3)(py)I]$ (165d, OY, 50)	A; Py (1 ml), 13, $CH_2Cl_2$ - diethyl ether	49.2 (49.6)	3.9 (3.7)	2.0 (2.1)	19.4 (18.8)	840	4.5
18.	$[(Cp)Ru(AsPh_3)(Bipy)]^+ I^-$ (250, O, 70)	A; Bipy (60), 15, $CHCl_3$ - diethyl ether	52.7 (52.5)	4.2 (3.7)	3.4 (3.7)	16.0 (16.8)	845	4.6
19.	$[(Cp)Ru(AsPh_3)(o\text{-phen})]^+ I^-$ (250, O, 75)	A; o-phen (50), 15, $CHCl_3$ - diethyl ether	53.6 (53.9)	3.4 (3.6)	3.9 (3.6)	16.8 (16.3)	847	5.0
20.	$[(Cp)Ru(AsPh_3)(py)CN]$ (225, YG, 65)	A, Py (1 ml), 12, $CH_2Cl_2$ - light petroleum	60.1 (60.4)	4.7 (4.3)	4.6 (4.9)	-	840	4.6
21.	$[(Cp)Ru(AsPh_3)(\gamma\text{-pic})CN]$ (235d, YG, 55)	A; $\gamma$ -pic (1 ml), 12, $CH_2Cl_2$ -light petroleum	62.0 (61.1)	4.5 (4.6)	5.1 (4.8)	-	840 $\nu_{CN}$ 2050	4.6
22.	$[(Cp)Ru(AsPh_3)(Bipy)]^+ CN^-$ (250, OY, 60)	A; Bipy (60); 20; $CHCl_3$ - light petroleum	62.0 (62.4)	4.1 (4.3)	6.5 (6.4)	-	845 $\nu_{CN}$ 2060	4.8
23.	$[(Cp)Ru(AsPh_3)(o\text{-phen})]^+ CN^-$ (250, OY, 68)	A; o-phen (60), 20, $CHCl_3$ - light petroleum	63.2 (63.7)	4.3 (4.1)	6.2 (6.1)	-	845 $\nu_{CN}$ 2060	4.8
24.	$[(Cp)Ru(AsPh_3)(py)SnCl_3]$ (185, Y, 40)	A; Py (1 ml), 14, $CHCl_3$ - light petroleum	43.6 (43.3)	3.5 (3.2)	2.0 (1.8)	14.2 (13.7)	845	4.5

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Table IV.1 (contd.)

1	2	3	4	5	6	7	8
25.	$[(Cp)Ru(AsPh_3)(Bipy)]^+SnCl_3^-$ (225, OY, 50)	A; Bipy (60), 20, $CHCl_3$ - light petroleum	46.7 (46.2)	3.5 (3.3)	3.0 (3.3)	12.7 (12.4)	845 4
26.	$[(Cp)Ru(AsPh_3)(o-phen)]^+SnCl_3^-$ (227, OY, 60)	A; o-phen (60), 20, $CHCl_3$ - light petroleum	47.4 (47.9)	3.1 (3.2)	3.5 (3.2)	12.5 (12.0)	850 4
27.	$[(Cp)Ru(SbPh_3)(py)Cl]$ (185, 4, 50)	A; Py (1 ml), 10, evapora- tion under reduced pre- ssure, $CH_2Cl_2$ -petroleum ether	53.1 (53.2)	4.1 (4.0)	2.2 (2.0)	5.3 (5.5)	845 4
28.	$[(Cp)Ru(SbPh_3)(\gamma-pic)Cl]$ (260, Y, 50)	A; $\gamma$ -pic (1 ml), 10, evapo- ration under reduced pressure, $CH_2Cl_2$ -petro- leum ether	53.7 (53.8)	4.4 (4.2)	2.3 (2.2)	6.0 (5.4)	845 4
29.	$[(Cp)Ru(SbPh_3)(Bipy)]^+Cl^-$ (250, OY, 70)	A; Bipy (50, 15, $CHCl_3$ - ether	55.3 (55.8)	3.5 (3.9)	4.0 (3.9)	5.2 (4.9)	850 4
30.	$[(Cp)Ru(SbPh_3)(o-phen)]^+Cl^-$ (255, O, 75)	A; o-phen (50), 15, EtOH- ether	57.6 (57.2)	3.8 (3.8)	4.0 (3.8)	4.2 (4.8)	850 4
31.	$[(Cp)Ru(SbPh_3)(py)Br]$ (185d, Y, 40)	A; Py (1 ml), 12, $CH_2Cl_2$ - light petroleum	49.1 (49.6)	3.2 (3.7)	2.0 (2.1)	12.4 (11.8)	845
32.	$[(Cp)Ru(SbPh_3)(Bipy)]^+Br^-$ (250, Y, 60)	A; Bipy (50), 15, EtOH- ether	51.7 (52.4)	4.5 (3.7)	3.6 (3.7)	11.1 (10.6)	850 4
33.	$[(Cp)Ru(SbPh_3)(o-phen)]^+Br^-$ (240, OR, 70)	A; o-phen (50), 15, $CHCl_3$ - ether	54.1 (53.9)	3.4 (3.6)	3.7 (3.6)	11.0 (10.3)	850 4

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Table IV.1 (contd.)

1	2	3	4	5	6	7	8
34.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{py})\text{I}]$ (160d, Y, 50)	A; Py (1 ml), 12, $\text{CH}_2\text{Cl}_2$ - light petroleum	46.9 (46.4)	4.2 (3.4)	2.2 (1.9)	18.2 (17.5)	850
35.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{Bipy})]^+\text{I}^-$ (235d, O, 60)	A; Bipy (50), 15, $\text{CHCl}_3$ - light petroleum	49.0 (49.3)	4.1 (3.5)	3.7 (3.5)	16.6 (15.8)	850
36.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{o-phen})]^+\text{I}^-$ (225, OR, 60)	A; o-phen (50), 15, $\text{CHCl}_3$ - light petroleum	50.2 (50.8)	4.0 (3.4)	3.2 (3.4)	16.2 (15.4)	850
37.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{py})\text{CN}]$ (225, Y, 60)	A; Py (1 ml), 13, $\text{CH}_2\text{Cl}_2$ - light petroleum	55.3 (55.8)	4.5 (4.0)	4.5 (4.5)	-	845
38.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{Bipy})]^+\text{CN}^-$ (242, OY, 70)	A; Bipy (50), 20, $\text{CHCl}_3$ - diethyl ether	58.0 (58.2)	3.5 (4.0)	6.2 (6.4)	-	850
39.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{o-phen})]^+\text{CN}^-$ (240, OY, 70)	A; o-phen (50), 20, $\text{CHCl}_3$ - diethyl ether	60.1 (59.6)	4.2 (3.9)	5.6 (5.8)	-	850
40.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{py})\text{NCS}]$ (193, OY, 50)	A; Py (1 ml), 12, $\text{CH}_2\text{Cl}_2$ - light petroleum	52.8 (53.0)	4.2 (3.8)	4.1 (4.3)	5.5 (4.9)	850 $\nu_{\text{CN}}$ 2030
41.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)\text{Bipy}]^+\text{NCS}^-$ (195, OY, 40)	A; Bipy (60), 15, $\text{CHCl}_3$ - light petroleum	55.3 (55.7)	4.3 (3.8)	5.9 (5.7)	5.0 (4.4)	850 $\nu_{\text{CN}}$ 2030
42.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{o-phen})]^+\text{NCS}^-$ (205, O, 60)	A; o-phen (60), 15, $\text{CHCl}_3$ - diethyl ether	56.7 (57.1)	4.1 (3.7)	5.4 (5.5)	4.8 (4.2)	850 $\nu_{\text{CN}}$ 2040
43.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{Py})(\text{SnCl}_3)]$ (215, Y, 50)	A; Py (2 ml), 15, $\text{CH}_2\text{Cl}_2$ - light petroleum	41.2 (40.9)	3.2 (3.1)	2.1 (1.7)	13.5 (12.8)	845

Table IV.1 (contd.)

1	2	3	4	5	6	7	8	9
44.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{Bipy})]^+\text{SnCl}_3^-$ (225, OY, 70)	A; Bipy (50), 24, $\text{CHCl}_3$ - diethyl ether	44.2 (44.0)	3.5 (3.1)	3.0 (3.1)	12.4 (11.8)	850	4.6
45.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{o-phen})]^+\text{SnCl}_3^-$ (180, OY, 60)	A; o-phen (60), 24, $\text{CHCl}_3$ - diethyl ether	44.8 (45.5)	3.5 (3.0)	3.2 (3.0)	12.0 (11.5)	850	4.57
46.	$[(\text{Cp})\text{Ru}(\text{AsPh}_3)(\text{Bipy})]^+\text{BPh}_4^-$ (250, OY)	B; $\text{NaBPh}_4$ (50), $\text{CHCl}_3$ - ethanol	71.5 (72.2)	5.7 (5.1)	3.0 (2.9)	-	850	
47.	$[(\text{Cp})\text{Ru}(\text{AsPh}_3)(\text{Bipy})]^+\text{BF}_4^-$ (260, OR)	B; $\text{NaBF}_4$ (40), $\text{CHCl}_3$ - ethanol	55.0 (55.4)	5.2 (3.9)	4.0 (3.9)	-	847	
48.	$[(\text{Cp})\text{Ru}(\text{AsPh}_3)(\text{Bipy})]^+\text{HgCl}_3^-$ (260, R)	B; $\text{HgCl}_2$ (50, ca. 0.2 mmol), refluxed for 10 min., $\text{CHCl}_3$ -ethanol	42.6 (42.3)	3.7 (3.0)	3.1 (3.0)	11.7 (11.3)	850	
49.	$[(\text{Cp})\text{Ru}(\text{AsPh}_3)(\text{Bipy})]_2^+\text{Zn}_2\text{Cl}_6^{2-}$ (280, R)	B; $\text{ZnCl}_2$ (50) refluxed for for 10 min., $\text{CHCl}_3$ - ethanol	49.3 (49.5)	4.1 (3.5)	3.4 (3.5)	14.0 (13.3)	845	
50.	$[(\text{Cp})\text{Ru}(\text{AsPh}_3)(\text{o-phen})]^+\text{BPh}_4^-$ (260, OR)	B; $\text{NaBPh}_4$ (50), $\text{CHCl}_3$ - ethanol	72.2 (72.9)	5.6 (5.0)	3.1 (2.9)	-	850	
51.	$[(\text{Cp})\text{Ru}(\text{AsPh}_3)(\text{o-phen})]^+\text{BF}_4^-$ (250, R)	B; $\text{NaBF}_4$ (40), $\text{CHCl}_3$ - ethanol	56.7 (56.8)	4.2 (3.8)	3.6 (3.8)	-	847	
52.	$[(\text{Cp})\text{Ru}(\text{AsPh}_3)(\text{o-phen})]^+\text{HgCl}_3^-$ (270, R, 80)	B; $\text{HgCl}_2$ (30), refluxed 10 min., $\text{CHCl}_3$ -ethanol	43.5 (43.8)	3.5 (2.9)	3.2 (2.9)	11.7 (11.1)	850	
53.	$[(\text{Cp})\text{Ru}(\text{AsPh}_3)(\text{o-phen})]_2^+\text{Zn}_2\text{Cl}_6^{2-}$ (280, R, 80)	B; $\text{ZnCl}_2$ (40), refluxed for 10 min., $\text{CHCl}_3$ - ethanol	50.3 (51.0)	3.4 (3.4)	3.1 (3.4)	13.5 (12.9)	850	
54.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{Bipy})]^+\text{BPh}_4^-$ (250, OR)	B; $\text{NaBPh}_4$ (50), $\text{CHCl}_3$ - ethanol	67.5 (68.8)	4.7 (4.6)	2.7 (2.8)	-	850	4.2

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Table IV.1- (contd.)

1	2	3	4	5	6	7	8	9
55.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{Bipy})]^+(\text{Bipy})^+\text{BF}_4^-$ (260, R)	B; $\text{NaBF}_4$ (30), $\text{CHCl}_3$ -ethanol	51.5 (52.0)	3.7 (3.7)	3.6 (3.7)	-	850	
56.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{Bipy})]^+\text{HgCl}_3^-$ (260, R, 80)	B; $\text{HgCl}_2$ (50), the reaction mixture was refluxed for 10 min., $\text{CHCl}_3$ -ethanol	39.7 (40.3)	4.0 (2.8)	3.1 (2.8)	11.2 (10.5)	850	
57.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{Bipy})_2]^{2+}\text{Zn}_2\text{Cl}_6^{--}$ (280, R, 80)	B; $\text{ZnCl}_2$ (50), the reaction mixture was refluxed for 10 min., $\text{CHCl}_3$ -ethanol	47.2 (46.7)	3.5 (3.3)	3.2 (3.3)	13.0 (12.5)		
58.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{o-phen})]^+\text{BPh}_4^-$ (245, R)	B; $\text{NaBPh}_4$ (40), $\text{CHCl}_3$ -ethanol	69.6 (69.5)	5.3 (4.7)	2.5 (2.7)	-		
59.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{o-phen})]^+\text{BF}_4^-$ (250, R)	B; $\text{NaBF}_4$ (30), $\text{CHCl}_3$ -ethanol	53.1 (53.4)	4.2 (3.6)	3.6 (3.6)	-		
60.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{o-phen})]^+\text{HgCl}_3^-$ (260, R, 80)	B; $\text{HgCl}_2$ (40), the reaction mixture was refluxed for 10 min., $\text{CHCl}_3$ -	41.3 (41.7)	3.0 (2.1)	3.1 (2.8)	11.3 (10.5)		
61.	$[(\text{Cp})\text{Ru}(\text{PPh}_3)(\text{acac})]$ (140d, 80, 50)	A; acac (5 ml), $\text{CH}_2\text{Cl}_2$ -ether; After evaporation of the solvent red oil was formed. The red oil washed with light petroleum, several times.	63.2 (63.7)	5.6 (5.1)	-	-	840	4.3
62.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{acac})]$ (160d, R, 50)	A; acac (5 ml), $\text{CH}_2\text{Cl}_2$ -ether	54.6 (54.3)	4.1 (4.5)	-	-	840	4.5
63.	$[(\text{Cp})\text{Ru}(\text{SbPh}_3)(\text{DTC})]$ (155, 0, 50)	A; DTC (25 mg), $\text{CH}_2\text{Cl}_2$ -petroleum ether	50.1 (50.4)	4.4 (4.5)	2.0 (2.1)	10.0 (9.6)	840	4.27



Table IV.1 (contd.)

\* A/B = method ; S = substrate; T = time; R' = recrystallization of complex; Cp = ( $\eta$ -C<sub>5</sub>H<sub>5</sub>).

a, Melting points (uncorrected).

b, R = red, Y = yellow, O = orange, YG = yellowish green, OR = orangish-red, BO = brownish orange.

c, Solvent CCl<sub>3</sub>. Aromatic protons of the other coligands appeared in the region  $\delta$  7.0-8.5 as broad multiplets, and in the case of  $\gamma$ -picoline, dithiocarbamate and acetylacetonate complexes additional signals in the region  $\delta$  1.8-2.5 were observed due to methyl protons.

d, decomposed.

e, Found: Mass 922, required: 924 (Mass spectrometry FD).

Fig. 4.1 Proposed structures of the complexes

IR SPECTRA OF THE COMPLEXES

Fig. 4.2 (a)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{Py})\text{Cl}]$

(b)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{Py})\text{CN}]$

(c)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\gamma\text{-pic})\text{CN}]$

Fig. 4.3  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{Bipy})]\text{Cl}$

Fig. 4.4 (a)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{o-phen})]\text{Cl}$

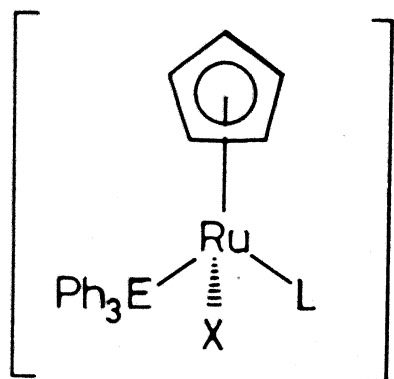
(b)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{Bipy})]\text{CN}$

Fig. 4.5 (a)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)(\text{Bipy})]\text{Cl}$

(b)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)(\text{o-phen})]\text{NCS}$

(c)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)(\text{o-phen})]\text{CN}$

(d)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)(\text{dte})]$

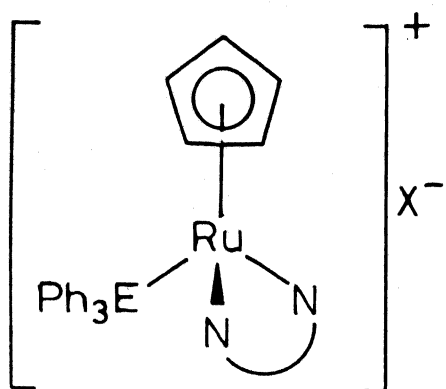


$X = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-, \text{NCS}^-$   
and  $\text{SnCl}_3^-$

$L = \text{Pyridine}, 4\text{-Picoline}$

$E = \text{As or Sb}$

Fig. 4.1(a)

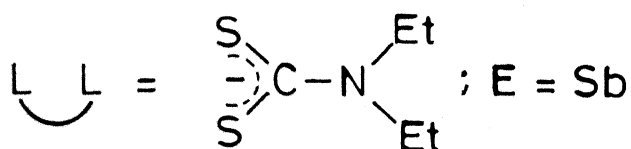


$X^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-, \text{NCS}^-$ ,  
 $\text{SnCl}_3^-$ ,  $\text{BPh}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$  or  
 $\text{HgCl}_3^-$

$\text{N} \text{---} \text{N} = 2, 2'\text{-Bipyridine}$   
or  $1, 10\text{-Phenanthroline}$

$E = \text{As or Sb or P}$

Fig. 4.1(b)



$E = \text{Sb}$

$L \text{---} L = \text{Acac}^-$ ;  $E = \text{P or Sb}$

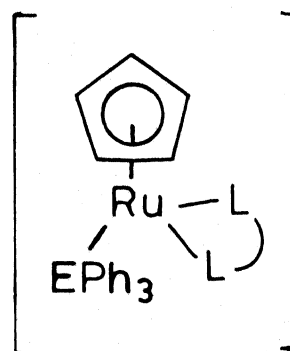


Fig. 4.1(c)

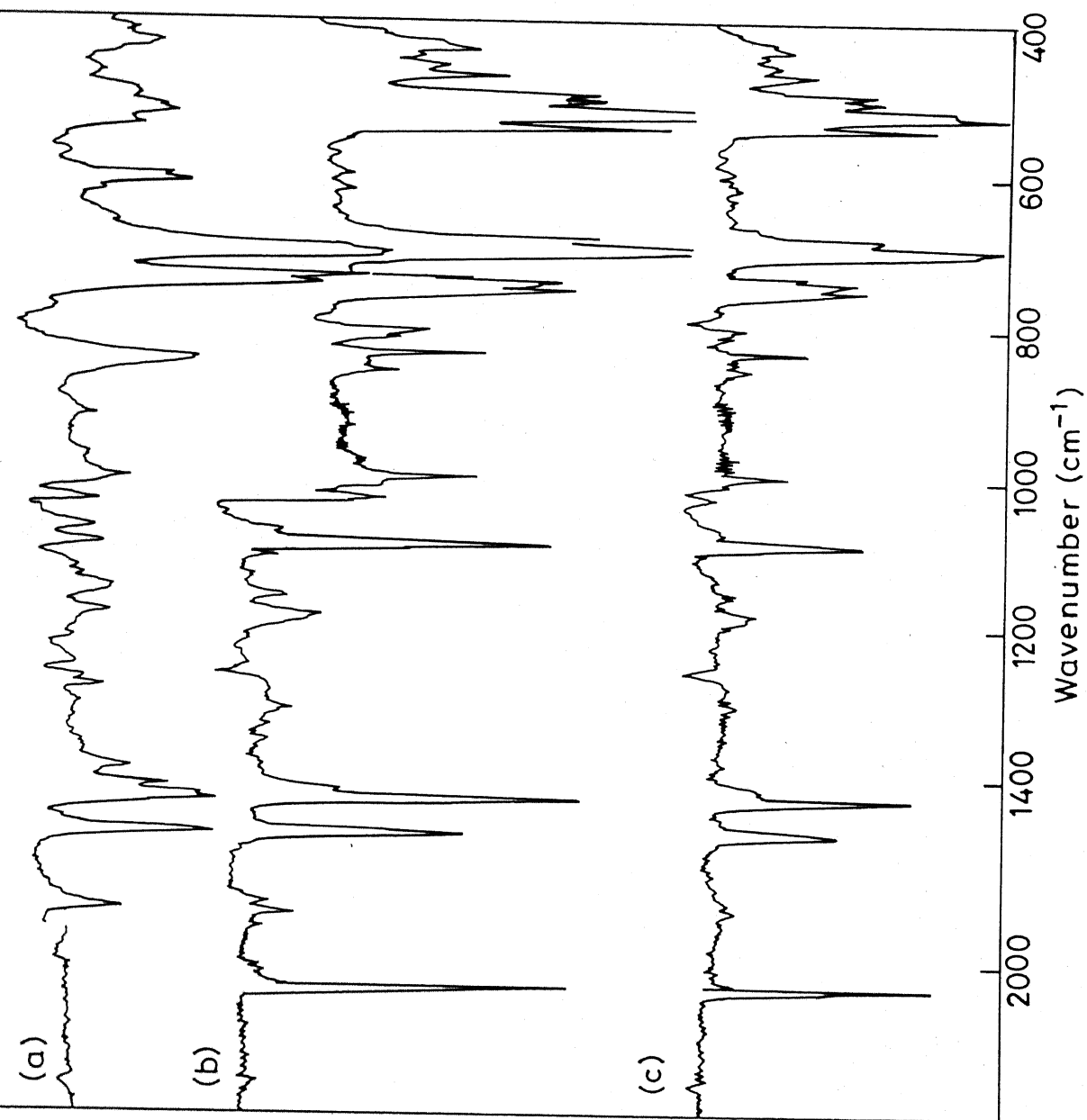


Fig. 4.2 Infrared spectra .

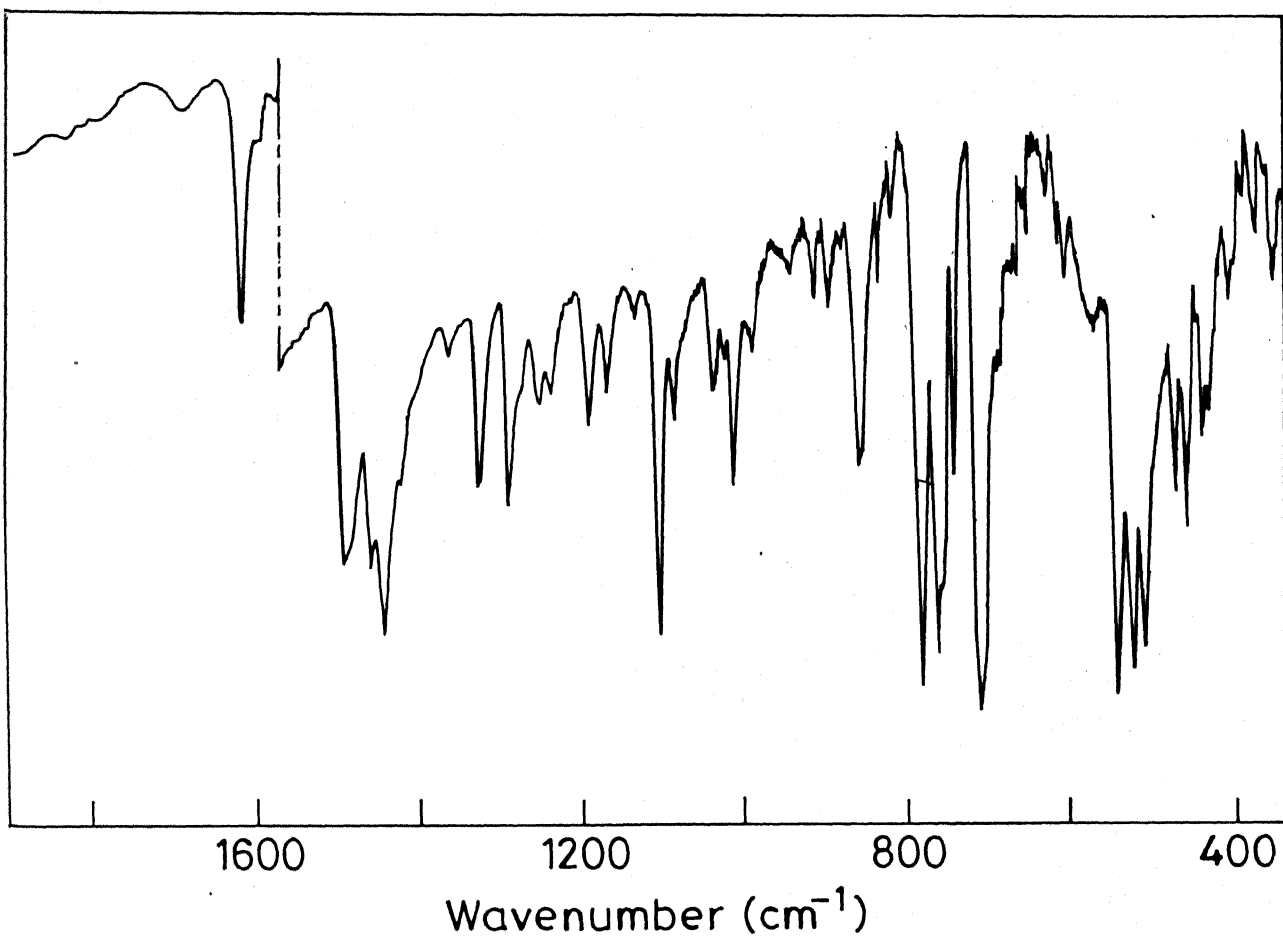


Fig. 4.3 Infrared spectrum.

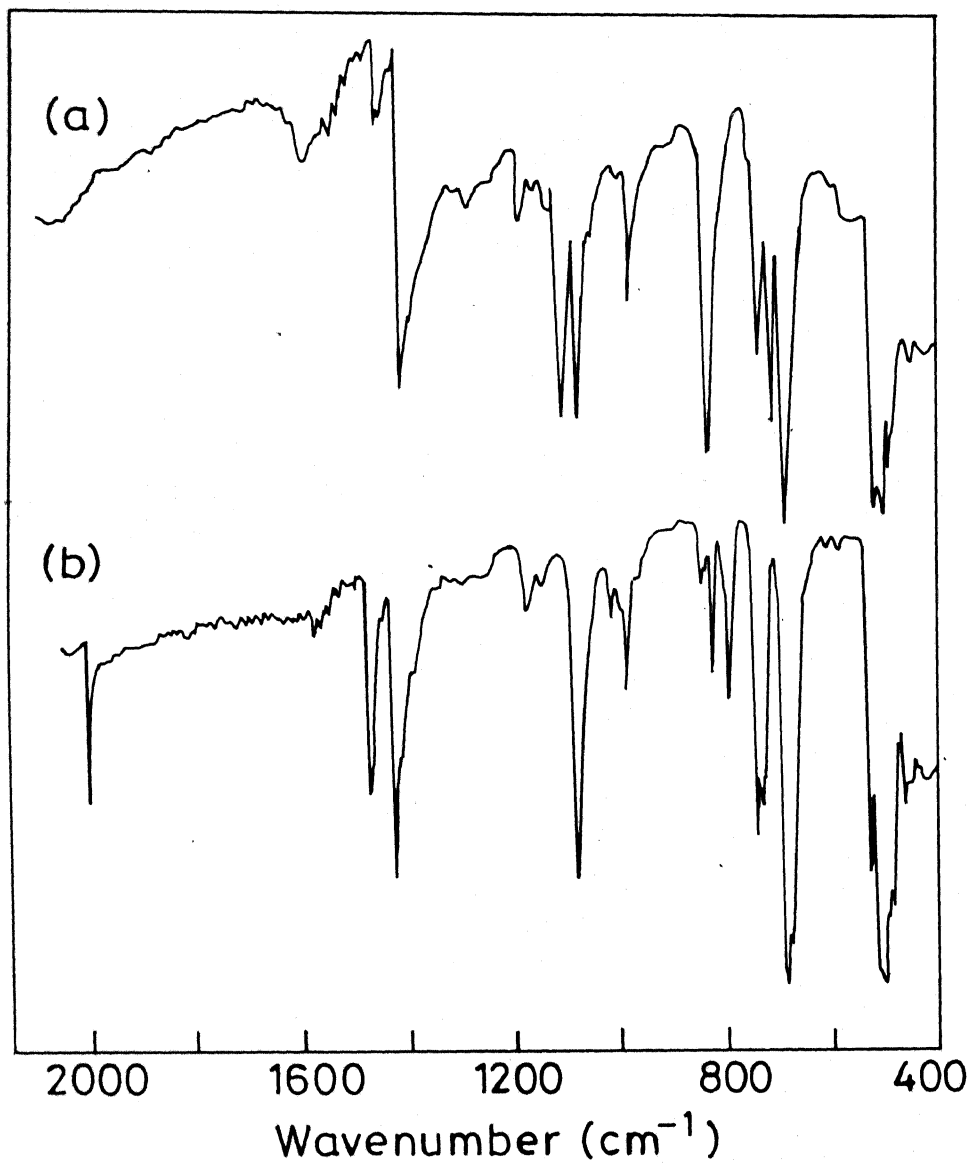


Fig. 4.4 Infrared spectra.

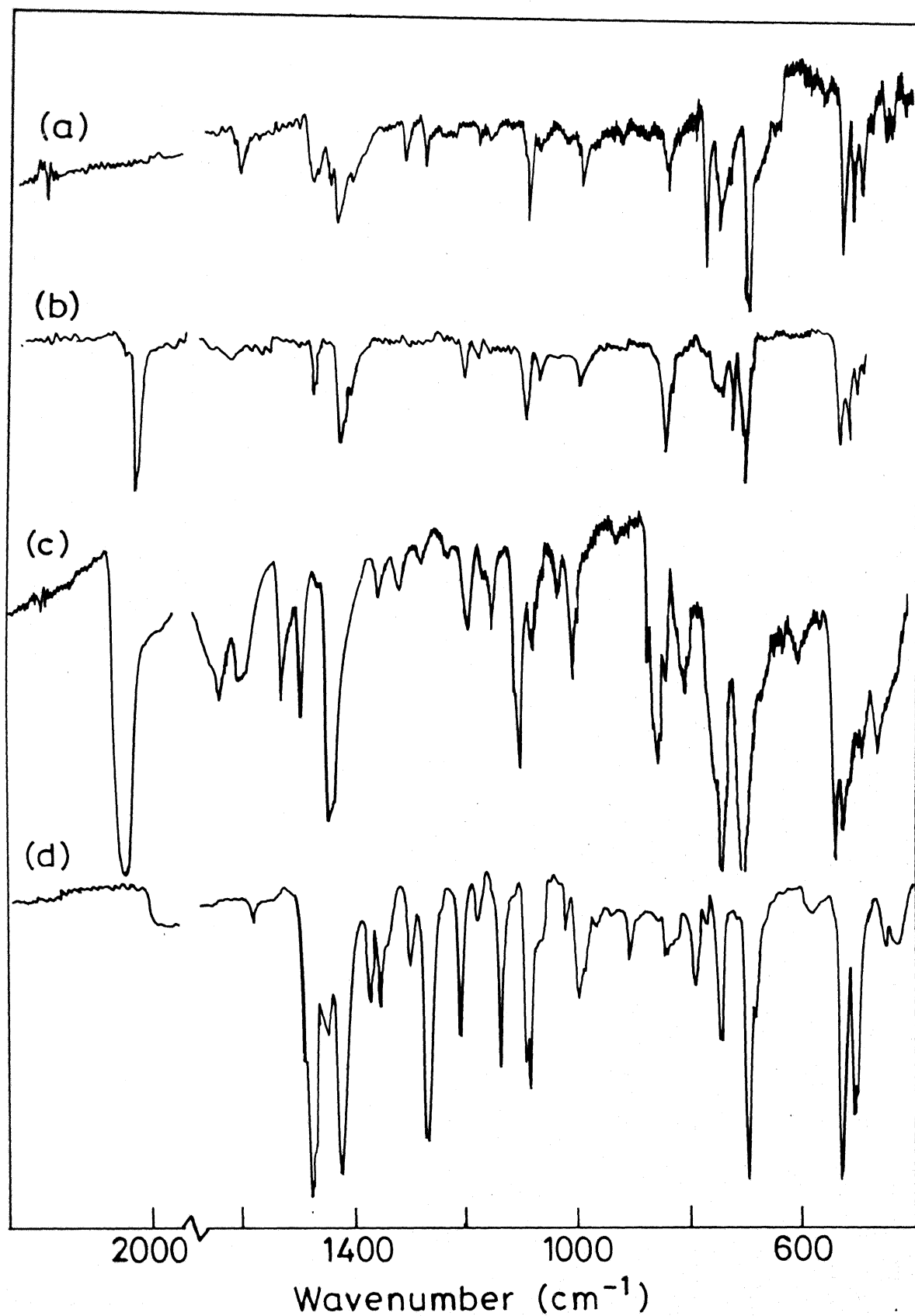


Fig. 4.5 Infrared spectra.

<sup>1</sup>H NMR SPECTRA OF THE COMPLEXES

Fig. 4.6 (a)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{Py})\text{CN}]$

(b)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)(\text{Py})\text{Cl}]$

(c)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)(\text{Py})\text{CN}]$

(d)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)\text{SnCl}_3(\text{Py})]$

Fig. 4.7 (a)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{Bipy})]\text{Br}$

(b)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)(\text{Bipy})]\text{CN}$

(c)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)(\text{Bipy})]\text{SnCl}_3$

Fig. 4.8 (a)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)(\text{o-phen})]\text{Br}$

(b)  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)(\text{o-phen})]\text{SnCl}_3$

Fig. 4.9  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)(\text{dtc})]$



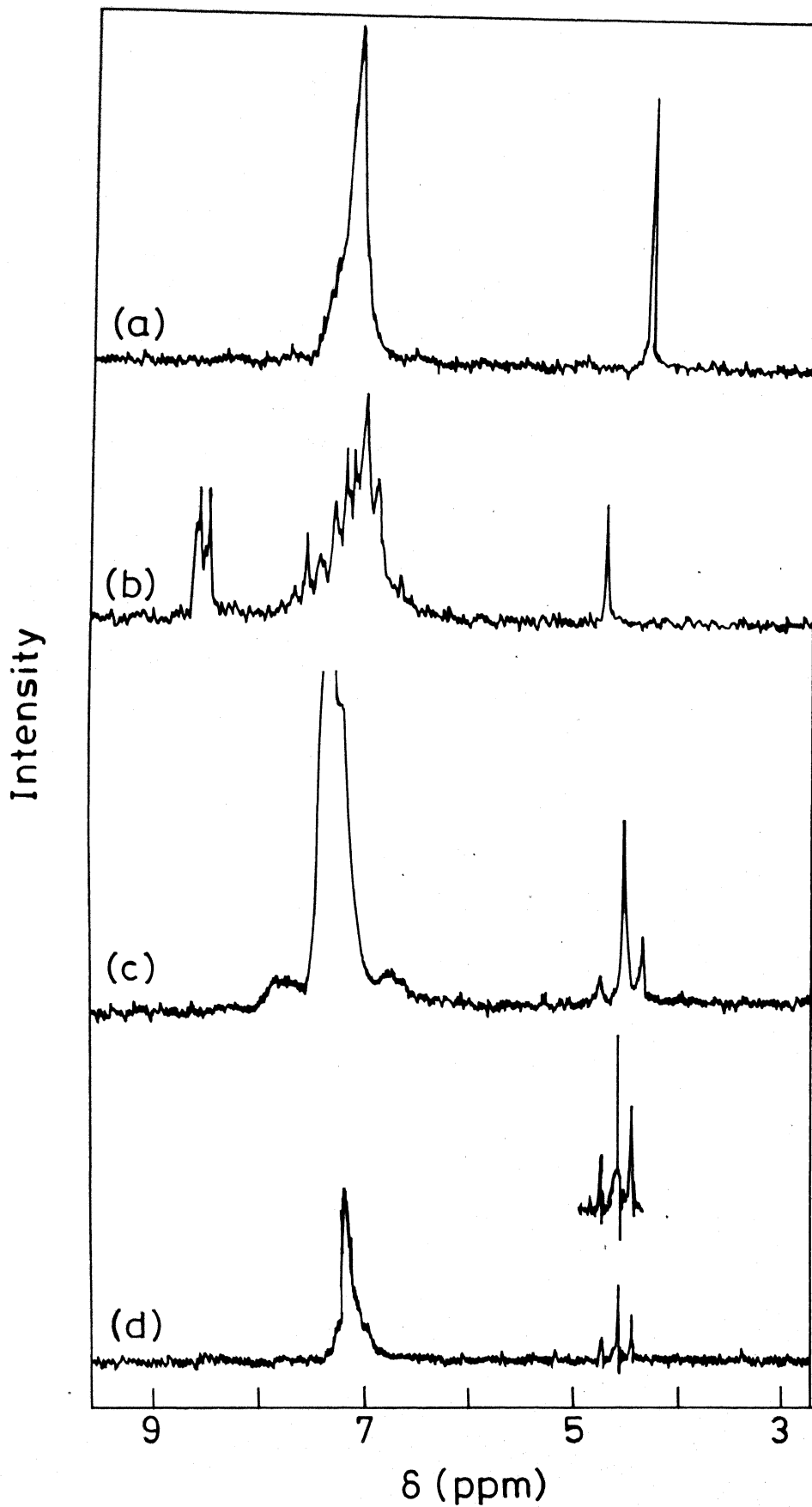


Fig. 4.6  $^1\text{H}$  NMR spectra

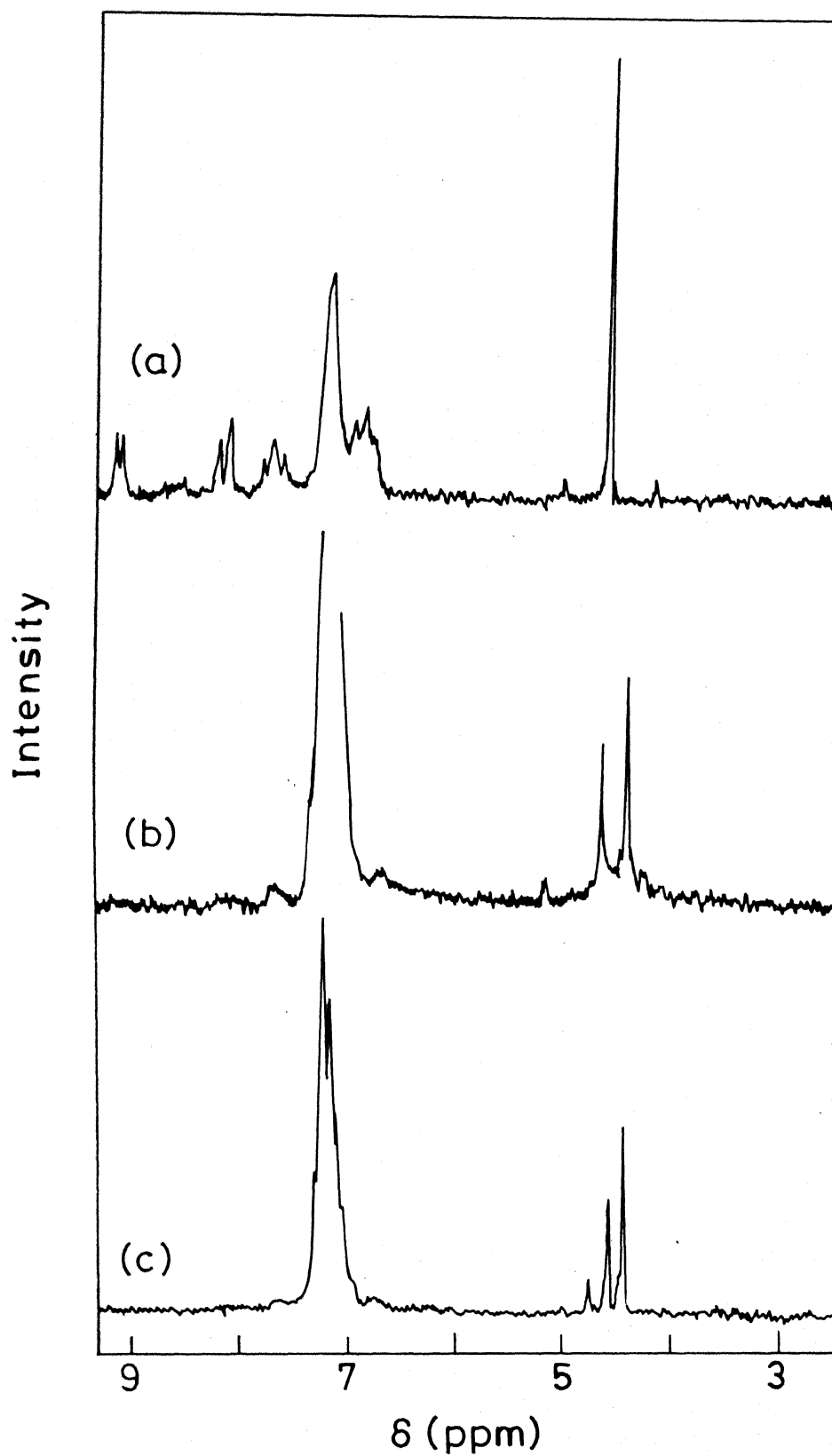


Fig. 4.7  $^1\text{H}$  NMR spectra .

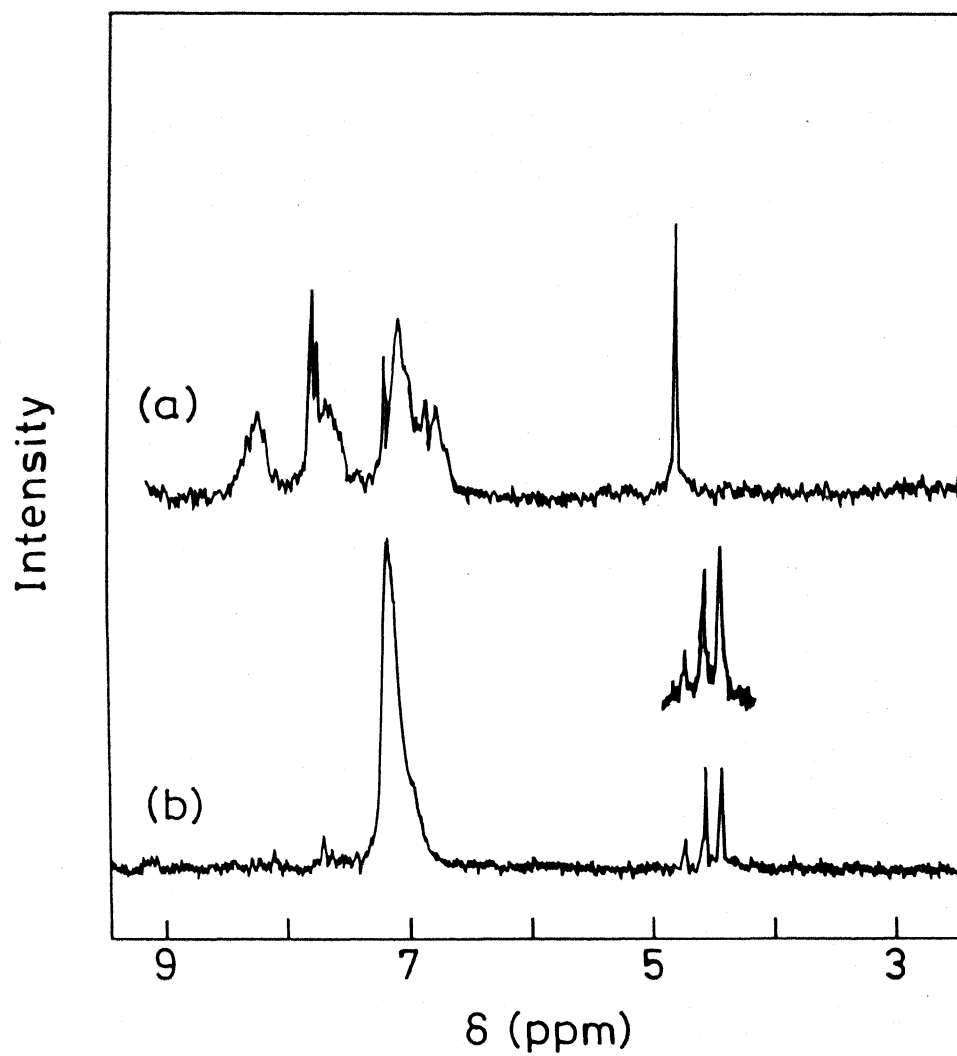


Fig. 4.8  $^1\text{H}$  NMR spectra.

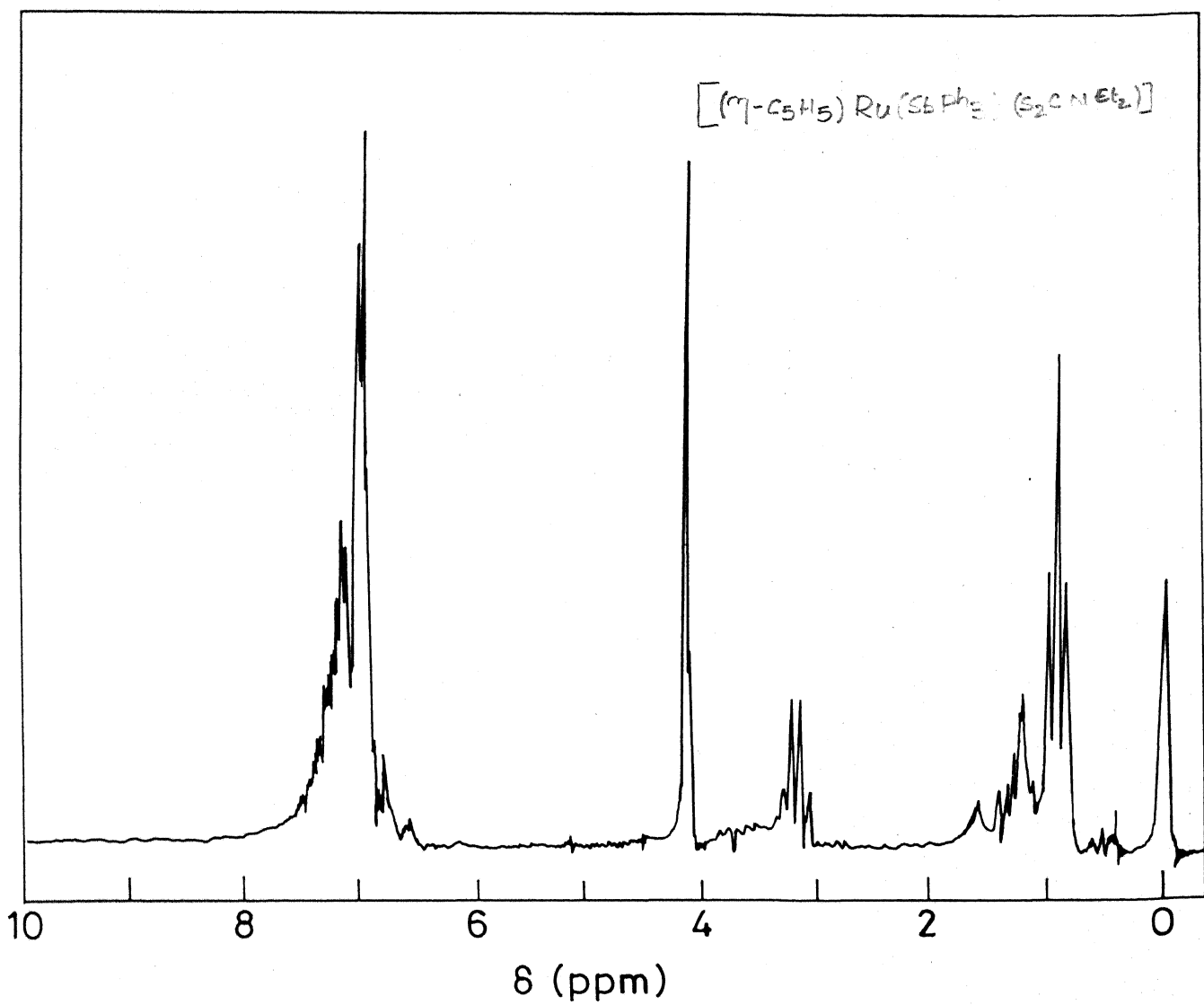


Fig. 4.9  $^1\text{H}$  NMR spectrum.

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## Chapter V

### SYNTHESIS OF BIMETALLIC CYANO-BRIDGED CATIONS CONTAINING CYCLOPENTADIENYL RUTHENIUM(II)

#### Introduction

Cyano-bridged cations  $[M-CN-M]^+$  of transition metals have been of interest for several years.<sup>1-4</sup> There has been some indication in the literature about the nucleophilic character of the cyano group in the complex  $[(\eta-C_5H_5)Ru(PPh_3)_2(CN)]$  which undergoes reactions with weak electrophiles like alkyl halides to yield the corresponding isonitrile cations  $[(\eta-C_5H_5)Ru(PPh_3)_2(CNR)]^+$ .<sup>5,6</sup> Further anticipation in this direction led to the utilization of this nucleophilicity to provide a general synthetic route for the cyano-bridged complexes by the interaction of  $[(\eta-C_5H_5)Ru(PPh_3)_2(CN)]$  with suitable organometallic halogeno complexes. As an extension of the same idea, we report herein the results of the reaction of  $[(\eta-C_5H_5)RuL_2(CN)]$  with  $[(\eta-C_5H_5)Ru(Cl)L_2]$  where  $L = PPh_3, AsPh_3, SbPh_3$ .

## Experimental

Spectra were obtained with Perkin-Elmer 1320 spectrophotometer (IR) and Bruker WP-80 ( $^1\text{H}$  NMR at 80 MHz) instruments. IR spectra were taken as KBr pellets. NMR spectra were taken in  $\text{CDCl}_3$  solution and TMS as internal reference. The elemental analyses were performed in the Microanalytical laboratory of the I.I.T., Kanpur. Melting points were taken on Fisher-Johns Melting point apparatus and are uncorrected.

The cyano- and halo-complexes were prepared by the literature methods.<sup>7-9</sup> The results are given in Table V.1.

## Preparation of Complexes

A typical reaction procedure is as under. The rest of the reactions were carried out by the same method (cf. Table V.1).

Suspension of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{Cl})\text{L}_2]$  (0.5 mmol),  $[(\eta\text{-C}_5\text{H}_5)\text{Ru-L}_2(\text{CN})]$  (0.5 mmol) ( $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$ ) and  $\text{NaBF}_4$  (ca. 1 mmol) in twice distilled methanol (30 ml) was first stirred for 1 to 2 hr at  $50^\circ\text{C}$  to give an orange coloured solution from which yellow crystals were precipitated after subsequent stirring the solution for one more hour at room temperature. It was separated by filtration and the precipitate washed with methanol. It was redissolved in  $\text{CH}_2\text{Cl}_2$  and the solution was centrifuged. Excess of light petroleum ( $40\text{-}60^\circ$ ) was added to the centrifugate whereby a pale yellow microcrystalline product was precipitated out. It was separated by filtration and the solid product was



dissolved in the minimum quantity of  $\text{CHCl}_3$  and applied onto a column of silica gel (50 cm x 1.5 cm). The elution was carried out with methanol-chloroform mixture (2:1). The first yellow band constituting the major reaction product was eluted as a yellow solution which was evaporated under low pressure whereby a pure yellow crystalline product was obtained. It was dried under vacuum (yield: 70-90%).

### Results and Discussion

Stirring of the cyano complexes with chloro complexes in the presence of  $\text{NaBF}_4$  in methanol at  $50^\circ\text{C}$  for two hours resulted in the formation of the crystalline diruthenium cyano-bridged cations  $[(\eta\text{-C}_5\text{H}_5)(\text{EPh}_3)_2\text{Ru-CN-Ru}(\eta\text{-C}_5\text{H}_5)(\text{EPh}_3)_2]^+$  (1-19). During the formation of these complexes the disappearance of the parent orange halo complexes with subsequent precipitation of yellow crystalline compounds eliminates the possibility of mixture of the starting material in the final yellow products. This possibility was further eliminated by the absence of even a trace of halide in the product and by the study of their proton NMR spectra as discussed later. It appears that along with the bridged complexes a little quantity of another cationic complex (ca. 10%) which remained on the silica gel column as a second band was also formed. The dimetallic cations 1-19 were characterized by chemical analyses, proton NMR and IR spectral methods. They all exhibited an IR band at 2080 assigned to  $\nu(\text{C}\equiv\text{N})$  (Fig. 5.1).

The position of the band is slightly higher than the one observed in the corresponding mononuclear complexes [ $\nu(\text{C}\equiv\text{N})$ , 2050  $\text{cm}^{-1}$ ]. This type of increase in the CN stretching frequency upon forming complexes containing bridging cyanide ligands from terminal cyano complexes has been documented by Wilmarth et al.<sup>10</sup> and has since been found to be a general phenomenon. This behaviour is taken here as a justification for the formation of these dimers as cyano bridged bimetallic complexes.

Proton NMR spectra of all cations except those containing  $\text{SbPh}_3$  ligands showed two cyclopentadienyl signals besides the ones due to phenyl protons of  $\text{EPh}_3$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ ) (Figs. 5.2 and 5.3). One could, however, assign these two signals to the protons of the starting material rather than a single complex in the yellow crystalline product. But the nmr spectra of the mixture of halo and cyanide exhibited pattern of the signals of  $\eta\text{-C}_5\text{H}_5$  protons different from the bridged cyano products (Fig. 5.4) suggesting the absence of the starting complexes in the product. Spectra of stibine complexes each  $\eta\text{-C}_5\text{H}_5$  proton singlet splits into two (Figs. 5.2 and 5.3) suggesting two different types of  $\eta\text{-C}_5\text{H}_5$  protons in them. Similar splits were also observed in the parent mononuclear complexes containing stibine.<sup>9</sup> It is surmized that non-equivalence of  $\eta\text{-C}_5\text{H}_5$  protons in the stibine complexes could either be caused by a possible slight tilt of  $\eta\text{-C}_5\text{H}_5$  ring towards one of the  $\text{SbPh}_3$  molecule in the complexes. So that the phenyl protons of  $\text{SbPh}_3$  interact with the  $\eta\text{-C}_5\text{H}_5$  protons or it

may be due to the hindered rotation of Ru- $\eta$ -C<sub>5</sub>H<sub>5</sub> bond because of the presence of bulky SbPh<sub>3</sub> ligands. There could, however, be other explanations for the splitting of  $\eta$ -C<sub>5</sub>H<sub>5</sub> protons and our explanation is purely tentative. Out of the two <sup>1</sup>H NMR signals in the PPh<sub>3</sub> and AsPh<sub>3</sub> complexes, the one that appeared at higher  $\delta$  value (low field side) is assigned to the  $\eta$ -C<sub>5</sub>H<sub>5</sub> which is linked to ruthenium bonded with the carbon of CN (Table V.1)

Although it will be difficult at this stage to assign any particular reason for this assignment but a highly speculative reason could be as follows. The carbon atom of the bridged cyanide group may be relatively less basic compared to that of the terminal CN resulting in lesser donation of electrons through  $\sigma$  bond to ruthenium. Furthermore Ru<sup>2+</sup> derived from (Table V.1) chloro complex may remove the antibonding  $\pi^*$  electrons from bonded CN.<sup>5</sup> This may lead to slight increase in the positive charge on ruthenium bonded to C of CN and consequently pull more of the  $\pi$ -electrons of  $\eta$ -C<sub>5</sub>H<sub>5</sub> towards ruthenium center resulting in the decrease to ring current of  $\eta$ -C<sub>5</sub>H<sub>5</sub> and shifting the nmr peak (due to <sup>1</sup>H) towards the higher-field side. The relative less basic character of carbon of the bridged CN could also explain the shift of  $\nu$ (CN) band position towards higher wave numbers. However, it is only a tentative explanation and more data is needed for a definite explanation.

The  $^1\text{H}$  NMR spectra of the complexes obtained prior to passing through the column showed another very weak band at  $\delta$  5.25 (cf. Fig. 5.3) representing  $\eta\text{-C}_5\text{H}_5$  protons bonded to ruthenium in the side product which has been removed by column chromatography. The high  $\delta$  value of the  $\eta\text{-C}_5\text{H}_5$  protons in the impurity suggests that the complex which is formed as a side product, must be cationic in nature.

For several dinuclear protons, there exists a possibility of the formation of different isomers if the scrambling of ligand L is allowed in solution. Such a possibility is however ruled out on the following grounds:

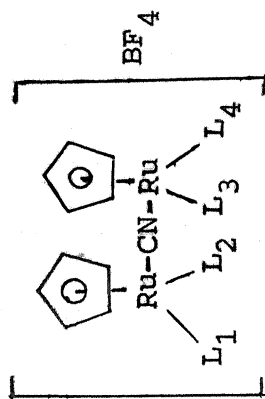
(1) We believe that the processes of dissociation and association of L in the complexes are kinetically controlled having very high activation energy. It takes nearly 24 hours in solvents like benzene for the substitution of one molecule of L in the complexes.<sup>9</sup> Since the time of reaction in the present syntheses is much too short (about 2 hr), the scrambling process by dissociation and subsequent substitution in polar solvents, is highly improbable.

(2) On the presumption of the scrambling process one would expect the presence of species like  $[(\eta\text{-C}_5\text{H}_5)\text{RuL}_x]^+$  ( $x = 1$  or  $2$ ) in solution. The latter will exhibit the signals for the  $\eta\text{-C}_5\text{H}_5$  protons on the lower field side (larger  $\delta$  value) in their NMR spectra besides the ones around  $\delta$  4.0 such signals

were not observed (Fig. 5.5).

(3) Though the difference in the position of  $\eta\text{-C}_5\text{H}_5$  protons in the dinuclear complexes with various L, is not large ( $\Delta\delta$  0.12 ppm) (Table V.1). One could, however, expect four signals due to  $\eta\text{-C}_5\text{H}_5$  protons if one takes the spectra of the mixture of two dinuclear complexes presuming no scrambling process taking place in solution. Nevertheless, such experiments have shown the presence of only two signals suggesting the scrambling process. The signals became slightly broad in a couple of cases. We, however, think that the presence of two signals is not an indication of the scrambling but is due to non-separation of four signals on account of a very small difference in the positions of proton signals in their spectra (0.1 ppm). The overlapping of signals could lead to broadening of the bands as was observed in a few cases (Fig. 5.5).

Table V.1



Sl. No.	Ligands*				Colour <sup>a</sup>	M.P. <sup>b</sup> (°C)	Time (hr)	IR (cm <sup>-1</sup> )	η-C <sub>5</sub> H <sub>5</sub> <sup>1</sup> H NMR <sup>c</sup>			Analyses: Found (Calcd.), %				
	L <sub>1</sub>	L <sub>2</sub>	L <sub>3</sub>	L <sub>4</sub>					1	2	10	11	12	C	H	N
1	2	3	4	5	6	7	8	9	10	11	12	13	14			
1.	P	P	P	P	GY	148	2	2060	4.18	4.06	67.3 (67.5)	4.8 (4.7)	1.12 (0.93)			
2.	P	P	P	Sb	Y	159	2	2070	4.21	4.12	64.76 (63.9)	5.4 (4.5)	1.0 (0.89)			
3.	P	P	As	P	GY	139	2	2080	4.21	4.09	62.5 (65.6)	5.8 (4.55)	2.2 (0.91)			
4.	P	P	As	As	GY	153	3	2070	4.15	4.03	59.4 (63.75)	5.2 (4.4)	1.3 (0.88)			
5.	P	P	Sb	Sb	PY	148	3	2080	4.18	4.06	61.0 (60.2)	5.4 (4.2)	1.5 (0.83)			
6.	As	P	P	P	GY	140	2	2080	4.18	4.06	66.6 (65.6)	5.5 (4.55)	2.2 (0.91)			

...contd.

Table V.1 (contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13	14
7.	As	P	As	P	Y	153	2	2080	4.18	4.05	62.6 (63.75)	4.7 (4.4)	1.21 (0.88)
8.	As	P	As	As	Y	151	3	2090	4.18	4.06	65.4 (62.0)	5.7 (4.31)	1.6 (0.86)
9.	As	P	Sb	Sb	PY	152	4	2060	4.18	4.06	58.4 (57.9)	4.3 (4.1)	0.92 (0.81)
10.	As	P	P	Sb	PY	155	2	2070	4.18	4.03	61.3 (61.9)	4.1 (4.3)	1.3 (0.86)
11.	As	As	P	P	Y	147	2	2080	4.18	4.06	63.48 (63.75)	4.7 (4.4)	1.2 (0.85)
12.	As	As	As	P	Y	153	3	2070	4.18	4.06	61.5 (62.0)	4.6 (4.31)	1.3 (0.86)
13.	As	As	As	As	Y	152	3	2070	4.18	4.06	60.1 (60.4)	4.51 (4.2)	1.1 (0.8)
14.	As	As	As	Sb	Sb	149	5	2080	4.15	4.03	57.0 (57.2)	5.1 (3.9)	1.3 (0.79)
15.	As	As	P	Sb	PY	155	4	2080	4.18	4.06	61.0 (60.1)	4.4 (4.1)	1.4 (0.8)
16.	Sb	Sb	P	P	PY	156	4	2095	4.39 4.30	4.27 4.09	61.2 (60.2)	4.5 (4.2)	1.2 (0.83)

...contd.

Table V.1 (contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13	14
17.	Sb	Sb	As	P	PY	154	5	2070	4.30	4.00	58.2	4.6	1.3
									4.21	3.90	(57.9)	(4.1)	(0.81)
18.	Sb	Sb	As	As	Y	155	5	2070	4.27	4.03	49.92	4.2	1.1
									4.15	3.87	(47.2)	(3.9)	(0.8)
19.	Sb	Sb	Sb	Sb	Y	157	5	2070	4.33	4.09	54.1	3.51	1.2
									4.21	3.90	(54.3)	(3.76)	(0.75)

\* P = PPh<sub>3</sub>; As = AsPh<sub>3</sub>; Sb = SbPh<sub>3</sub>.

a) Y = yellow; PY = pale yellow; GY = greenish yellow.

b) Melting points are uncorrected.

c) Solvent CDCl<sub>3</sub>. Aromatic protons of the other coligands appeared in the region  
 δ 7.0-8.0 as broad multiplets.



Fig. 5.1: IR SPECTRA OF THE COMPLEXES

- (a)  $[(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)(\text{PPh}_3)\text{Ru-CN-Ru}(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)(\text{PPh}_3)]\text{BF}_4$
- (b)  $[(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)_2\text{Ru-CN-Ru}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]\text{BF}_4$
- (c)  $[(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Ru-CN-Ru}(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)_2]\text{BF}_4$
- (d)  $[(\eta\text{-C}_5\text{H}_5)(\text{SbPh}_3)_2\text{Ru-CN-Ru}(\eta\text{-C}_5\text{H}_5)(\text{SbPh}_3)_2]\text{BF}_4$

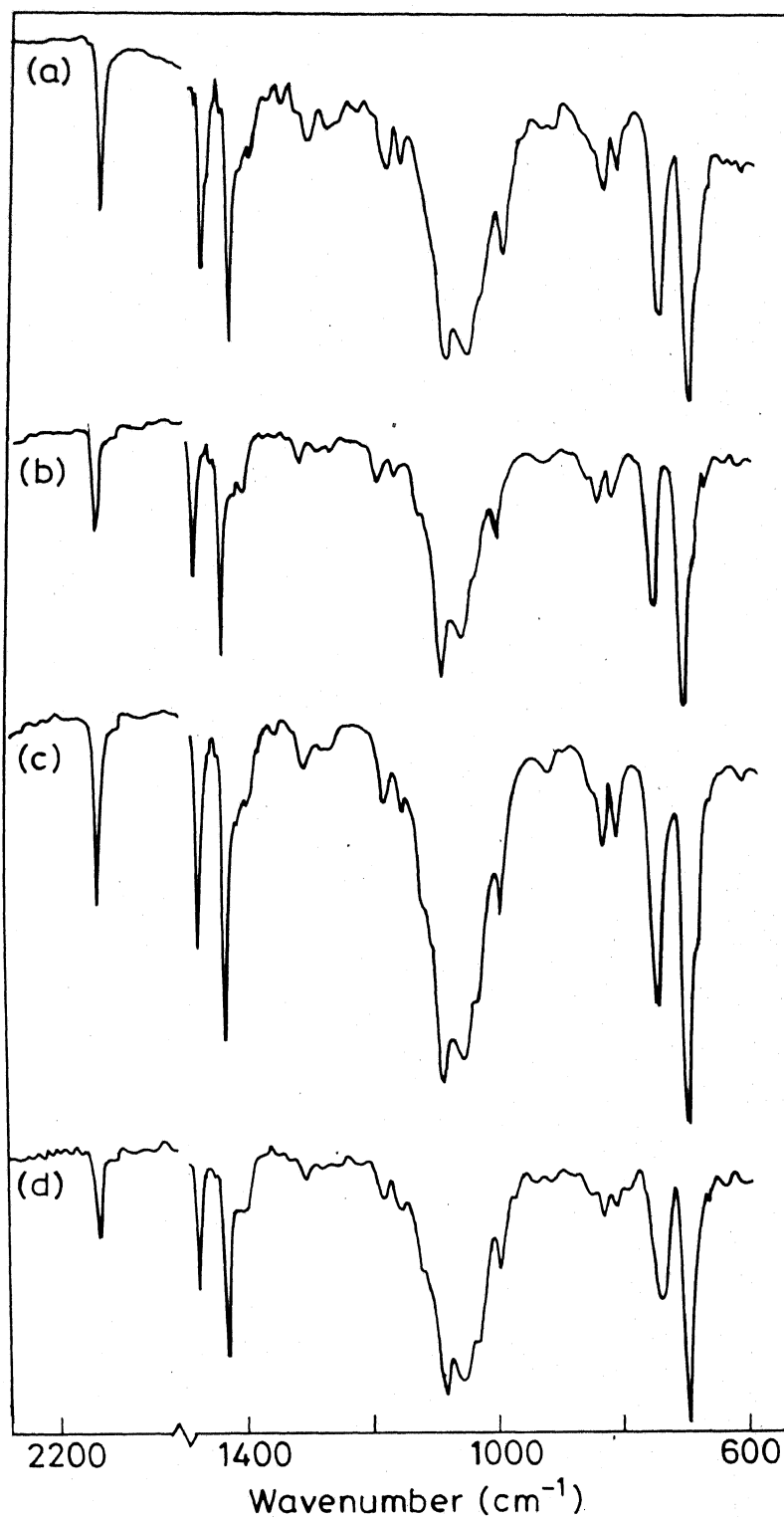


Fig. 5.1 Infrared spectra.

<sup>1</sup>H NMR SPECTRA OF THE COMPLEXES

Fig. 5.2

- (a)  $[(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)(\text{PPh}_3)\text{Ru-CN-Ru}(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)(\text{PPh}_3)]\text{BF}_4$
- (b)  $[(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Ru-CN-Ru}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{SbPh}_3)]\text{BF}_4$
- (c)  $[(\eta\text{-C}_5\text{H}_5)(\text{SbPh}_3)_2\text{Ru-CN-Ru}(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)_2]\text{BF}_4$
- (d)  $[(\eta\text{-C}_5\text{H}_5)(\text{SbPh}_3)_2\text{Ru-CN-Ru}(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)(\text{PPh}_3)]\text{BF}_4$

Fig. 5.3

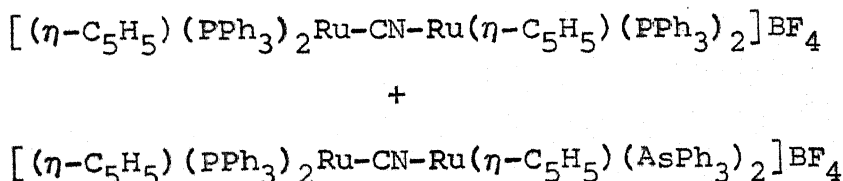
- (a)  $[(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)_2\text{Ru-CN-Ru}(\text{AsPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{BF}_4$
- (b)  $[(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)_2\text{Ru-CN-Ru}(\eta\text{-C}_5\text{H}_5)(\text{SbPh}_3)_2]\text{BF}_4$
- (c)  $[(\eta\text{-C}_5\text{H}_5)(\text{SbPh}_3)_2\text{Ru-CN-Ru}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]\text{BF}_4$
- (d)  $[(\eta\text{-C}_5\text{H}_5)(\text{SbPh}_3)_2\text{Ru-CN-Ru}(\eta\text{-C}_5\text{H}_5)(\text{SbPh}_3)_2]\text{BF}_4$

Fig. 5.4

- (a) Mixture of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{CN}] + [(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{AsPh}_3)_2\text{Cl}]$
- (b)  $[(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Ru-CN-Ru}(\eta\text{-C}_5\text{H}_5)(\text{AsPh}_3)_2]\text{BF}_4$
- (c) Mixture of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{SbPh}_3)_2\text{CN}] + [(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$
- (d)  $[(\eta\text{-C}_5\text{H}_5)(\text{SbPh}_3)_2\text{Ru-CN-Ru}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]\text{BF}_4$

Fig. 5.5

Mixture of dinuclear complexes of:



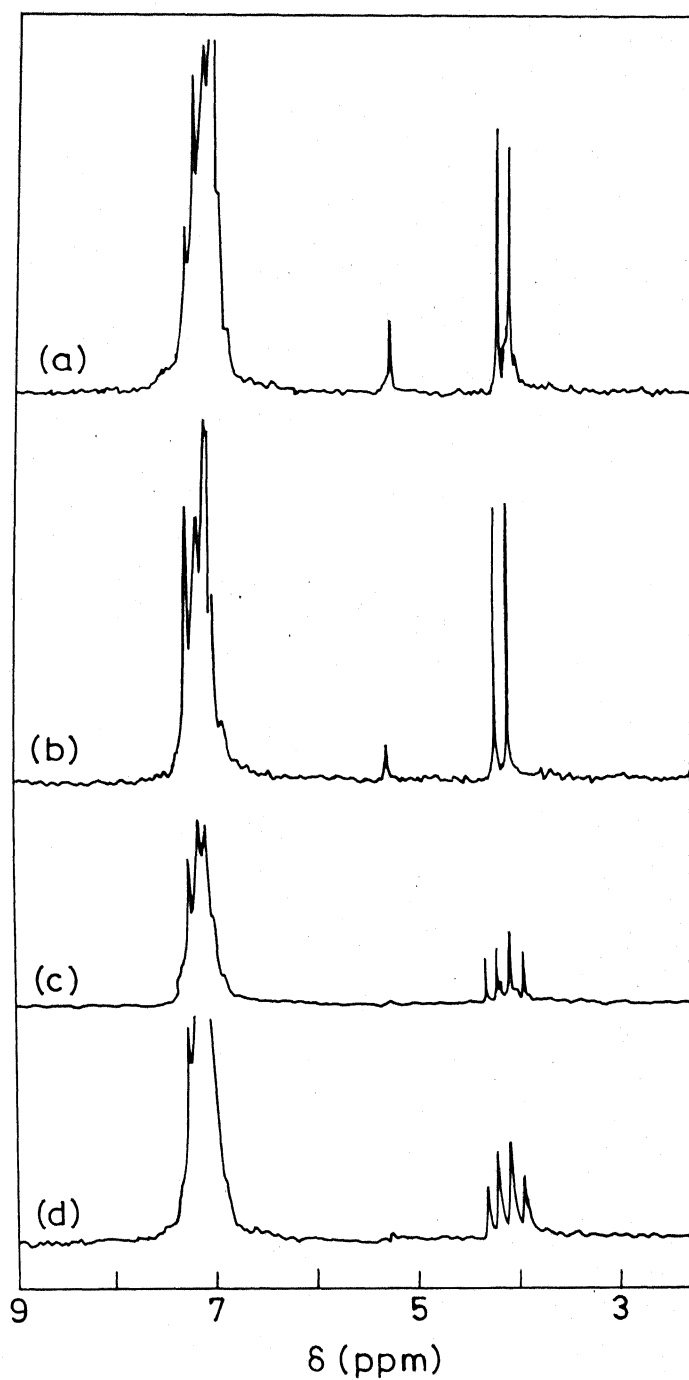


Fig. 5.2  $^1\text{H}$  NMR spectra.

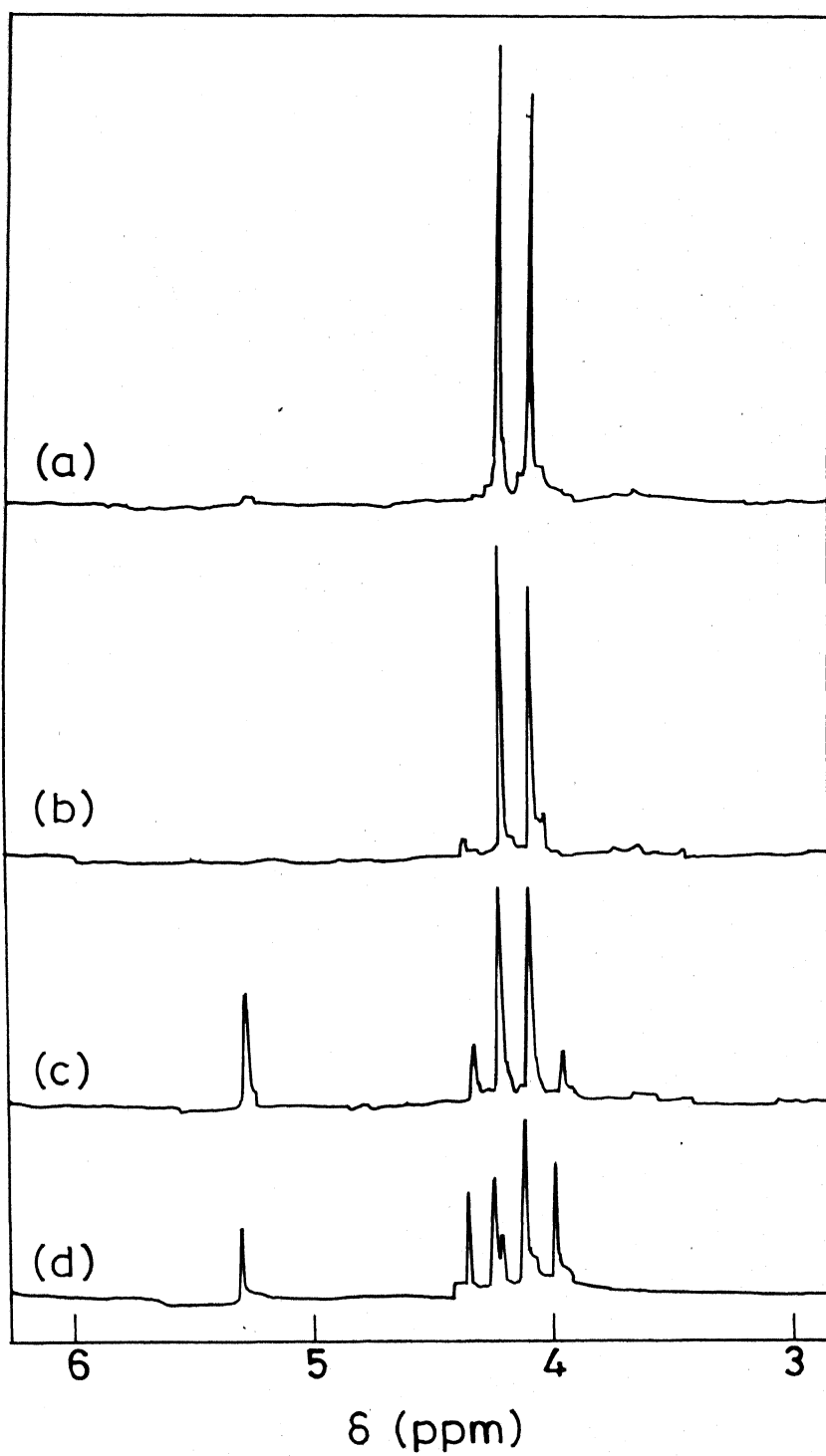


Fig. 5.3  $^1\text{H}$  NMR spectra.

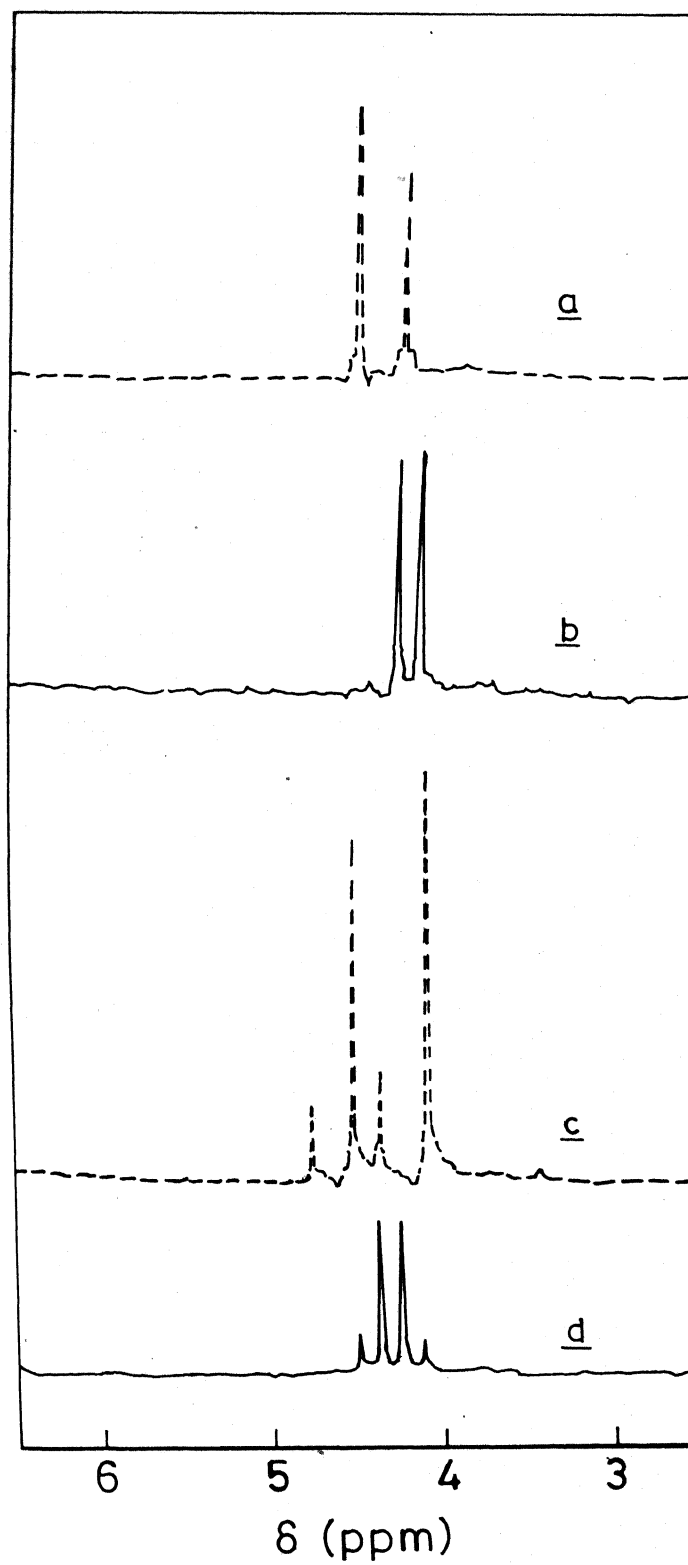


Fig. 5.4  $^1\text{H}$  NMR spectra

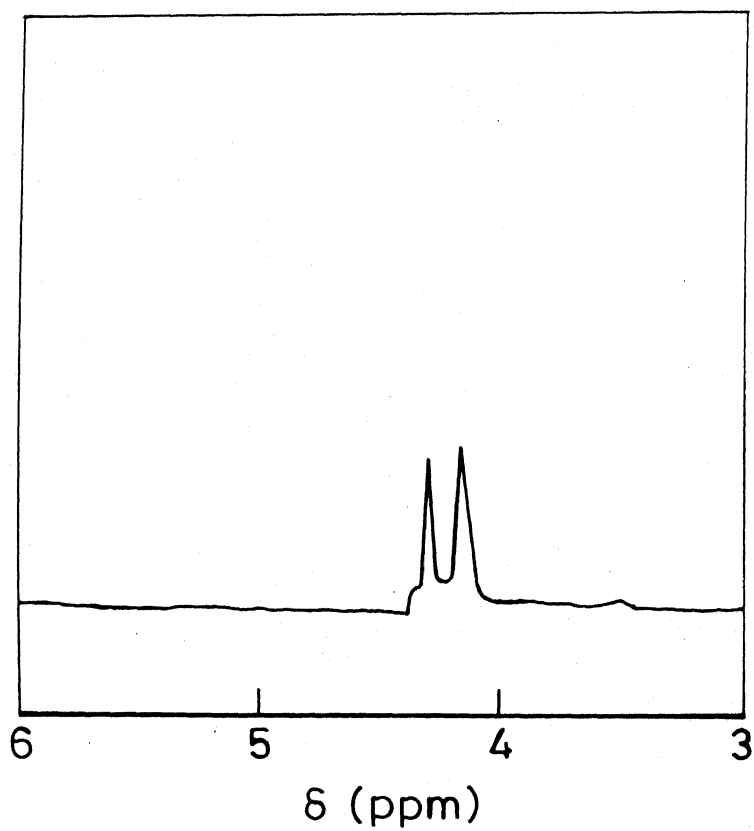


Fig. 5.5  $^1\text{H}$  NMR spectrum

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## Chapter VI

### STUDY OF THE REACTIONS OF SOME OF THE $\eta$ -CYCLOPENTADIENYL-RUTHENIUM(II) COMPLEXES WITH $\gamma$ -HYDROXYACETYLENES

#### Introduction

Although the field spanning the chemistry of the transition metal alkylidene (carbene) complexes is now well explored,<sup>1</sup> it is only in recent years that the reliable methods for the syntheses of metal complexes with unsaturated alkylidenes (vinylidene complexes  $M=C=CR_2$ ),<sup>2</sup> and allenylidene ( $M=C=C=CR_2$ )<sup>2a,3</sup> have developed, but their chemistry still remained largely unexplored. Selegue<sup>4,5</sup> reported the reaction between  $[(\eta-C_5H_5)-RuL_2Cl]$  and  $\gamma$ -hydroxyacetylenes which yielded allenylidene and dimeric vinylidenes. It appears that the formation of the alkylidene complexes depends largely upon the nature of the group substituted on  $\gamma$ -carbon. In spite of the work carried out in this direction, it will be interesting to extend the work further needed for exploring the latter field by reacting  $[(\eta-C_5H_5)RuL_2Cl]$  ( $L = PPh_3, AsPh_3, SbPh_3$ ) with various substituted acetylenes. We describe herein the results of the reactions of  $[(\eta-C_5H_5)-RuL_2Cl]$  with  $HC\equiv C-R$  ( $R = Ph, -CH_2OH, -CMe_2OH, -C(Me)(Et)OH, -C_6H_{10}OH, -C_6H_{10}Br, -CH_2OMe$ ).

## Experimental

General information regarding instrumentations and chemical analyses have already been given elsewhere.<sup>6</sup> Bruker WM-400 MHz spectrometer was used for taking the  $^{13}\text{C}$  NMR spectra of the complexes at 100 MHz in  $\text{CDCl}_3$ .

Complexes  $[(\eta\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$  ( $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$ ) were prepared by the literature methods.<sup>6a,7</sup>  $\gamma$ -Hydroxyacetylenes and phenylacetylene obtained from the commercial source (Aldrich) were used as such.

### General Procedure for Syntheses of the Complexes

(a) Preparation of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{C}=\text{C}=\text{CH}_2)\text{LL}']\text{BF}_4$  and  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{C}=\text{CHCH}_2\text{OH})\text{LL}']\text{BF}_4$  ( $\text{LL}' = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$ )

Addition of  $\text{NaBF}_4$  (ca. 0.05 g, 0.45 mmol) and  $\text{HC}\equiv\text{CCH}_2\text{OH}$  (ca. 0.1 mmol) to a suspension of  $[(\eta\text{-C}_5\text{H}_5)\text{RuLL}'\text{Cl}]$  (0.1 g, 0.12 mmol) in dry methanol (20 ml), followed by heating under reflux for a period (20 min.) yielded a deep red solution. It was filtered and evaporated to near dryness. The residue was extracted with  $\text{CH}_2\text{Cl}_2$  (10 ml) and centrifuged. Excess light petroleum (40-60°C) was added to the centrifugate which resulted in the precipitation of a reddish-tan complex. In order to purify the product, a solution of reddish-tan precipitate in  $\text{CH}_2\text{Cl}_2$  (5 ml) was absorbed on the top of a short silica column (2 cm x 10 cm). A mixture of  $\text{CH}_2\text{Cl}_2$  and acetone (4:1) was used


as an eluent. The first yellow fraction was collected and concentrated on water bath to about 10 ml. The complex was precipitated with light petroleum (40-60°), centrifuged, washed with petroleum ether, dried under vacuum and analysed for  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{C}=\text{C}=\text{CH}_2)\text{LL}']\text{BF}_4$  (yield: 80%).

The second fraction was collected as a violet coloured solution using  $\text{CH}_2\text{Cl}_2$ :acetone (3:2) as an eluent. The eluent was concentrated to one fourth its volume and the violet complex was precipitated with diethyl ether in about 10% yield. It was analysed for  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{C}=\text{CHCH}_2\text{OH})\text{LL}']\text{BF}_4$ .

The third fraction was collected as a green solution. It appeared to be a decomposed product and no attempt was therefore made to characterise it further.

(b) Preparation of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{C}=\text{C}=\text{C}_6\text{H}_{10})\text{LL}']\text{BF}_4$  ( $\text{LL}' = \text{PPh}_3$ ,  
 $\text{AsPh}_3$ ,  $\text{SbPh}_3$ )

A few drops of  $\gamma$ -hydroxyacetylene (1-ethyl-1-cyclohexanol) was added to a suspension of  $[(\eta\text{-C}_5\text{H}_5)\text{RuLL}'\text{Cl}]$  (0.12 mmol) and  $\text{NaBF}_4$  (0.50 mmol) in methanol (15 ml). The mixture was heated under reflux for 25 min, whereby the colour of the solution was changed to red. The resulting solution was centrifuged and the centrifugate was evaporated to near dryness under low pressure. The residue was adsorbed by transferring its solution in about 10 ml of  $\text{CH}_2\text{Cl}_2$  on the top of silica gel column (2 cm x 10 cm).

Elution with  $\text{CH}_2\text{Cl}_2$ :acetone (4:1) gave a major yellow fraction, from which a yellow compound was precipitated using light petroleum. Its recrystallisation with  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  afforded a yellow precipitate of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{C}=\text{C}=\text{C} \text{ )\text{LL}']\text{BF}_4$  (yield:80%).

A minor fraction collected as a green solution decomposed in the process of precipitation. Further attempts have not been made for isolating the product.

(c) Reactions of  $[(\eta\text{-C}_5\text{H}_5)\text{RuLL}'\text{Cl}]$  with  $\text{HC}\equiv\text{CC}_6\text{H}_{10}\text{Br}^8$  ( $\text{LL}' = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$ )

The reactions described in (b) were repeated by the same procedure using the corresponding bromoderivative of acetylene  $\text{HC}\equiv\text{C-C}_6\text{H}_{10}\text{Br}$  in place of hydroxy derivatives. The reaction product in every case invariably found to be the original reactants, viz.,  $[(\eta\text{-C}_5\text{H}_5)\text{RuL}_2\text{X}]$  even when the refluxing time was increased to a few hours.

(d) Preparation of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{C}=\text{CHPh})\text{LL}']\text{BF}_4$  ( $\text{LL}' = \text{AsPh}_3, \text{SbPh}_3$ ;  $\text{L} = \text{PPh}_3$ ;  $\text{L}' = \text{AsPh}_3$ )

Addition of  $\text{NaBF}_4$  (ca. 0.03 g, 0.23 mmol) and phenylacetylene (ca. 0.05 g, 0.5 mmol) to a suspension of  $[(\eta\text{-C}_5\text{H}_5)\text{-RuLL}'\text{Cl}]$  (ca. 0.15 g, 0.20 mmol) in dry methanol (15 ml), followed by heating the resulting solution for a brief period under reflux, gave a deep red solution. It was filtered and evaporated

to near dryness. The residue was extracted with dichloromethane (5-10 ml), and the extract was filtered into light petroleum (large excess) which yielded a reddish tan precipitate of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{C}=\text{CHPh})\text{LL}']\text{BF}_4$  (yield: 85%). The complex was purified by silica gel column (2 cm x 20 cm) using 9:1  $\text{CH}_2\text{Cl}_2$ : acetone mixture as eluent.

(e) Preparation of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{C}\equiv\text{C-R})\text{LL}']\text{BF}_4$  (R = Ph,  $-\text{CH}_2\text{OMe}$ ,  $-\text{C}\equiv\text{C}-(\text{CH}_2)_4$ ;  $\text{LL}' = \text{AsPh}_3, \text{SbPh}_3, \text{PPh}_3$ )

A mixture of  $[(\eta\text{-C}_5\text{H}_5)\text{RuLL}'\text{Cl}]$  (0.12 mmol) and a few drops of  $\gamma$ -hydroxyacetylenes (0.2 mmol) in methanol (10-15 ml) was heated under reflux for 20 min. Sodium borohydride (0.3 mmol) was added to the resulting solution whereby a yellowish crystalline compound was immediately separated in quantitative yield. The yellowish crystals were filtered, washed with methanol, diethyl ether and air dried. The complexes were recrystallised from  $\text{CHCl}_3/\text{MeOH}$  or  $\text{C}_6\text{H}_6/\text{MeOH}$  and analysed.

(f) Preparation of  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_{10}\text{H}_{11})\text{L}_4]\text{BF}_4$  (L =  $\text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$ )

A mixture  $[(\eta\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$  (0.5 g, 0.7 mmol),  $\text{NaBF}_4$  (ca. 0.2 g, 0.2 mmol) and  $\text{HC}\equiv\text{C-CMe}_2\text{OH}$  (ca. 0.4 ml, 0.53 mmol) in dry methanol (50 ml) was heated to reflux for 20 min. The resulting deep blue solution was filtered and evaporated to

near dryness. The residue was extracted with  $\text{CH}_2\text{Cl}_2$  (10 ml) and precipitated with light petroleum. The compound was recrystallised from  $\text{CH}_2\text{Cl}_2$ /diethyl ether to give deep blue complex  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_{10}\text{H}_{11})\text{L}_4]\text{BF}_4$  (yield: 95%).

(g) Preparation of  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_{12}\text{H}_{16})\text{L}_4]\text{BF}_4$  (L =  $\text{PPh}_3$ ,  $\text{AsPh}_3$ ,  $\text{SbPh}_3$ )

The reaction of  $\text{HC}\equiv\text{C}(\text{Me})(\text{Et})\text{OH}$  (0.4 ml, 0.5 mmol) in place of  $\text{HC}\equiv\text{CMe}_2\text{OH}$  with (0.5 g, 0.7 mmol) of  $[(\eta\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$  in the presence of  $\text{NaBF}_4$  (0.4 g, 0.4 mmol) by a method similar to that given in (f) yielded blue-violet coloured complex  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_{12}\text{H}_{16})\text{L}_4]\text{BF}_4$ , which was washed with light petroleum ether and recrystallised from  $\text{CH}_2\text{Cl}_2$ : ether (yield: 95%) and air dried.

(h) Preparation of  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_{10}\text{H}_{10}^{\text{M}})\text{L}_4]\text{Y}_2$  (L =  $\text{PPh}_3$ ,  $\text{AsPh}_3$ ,  $\text{SbPh}_3$ ; Y =  $\text{HgCl}_3$  or  $\text{Cu}_2\text{Cl}_2$ ; M =  $\text{CuCl}$  or  $\text{HgCl}$ )

A mixture of  $[(\eta\text{-C}_5\text{H}_5)\text{RuL}_2\text{Cl}]$  (ca. 0.5 g, 0.7 mmol),  $\text{HC}\equiv\text{CCMe}_2\text{OH}$  (ca. 0.35 ml, 0.52 mmol) and  $\text{HgCl}_2/\text{Cu}_2\text{Cl}_2$  (ca. 0.4 mmol) was heated under reflux for about 30 minutes. The resulting deep red solution was evaporated to near dryness under low pressure. The resulting residue was extracted with 10 ml of  $\text{CH}_2\text{Cl}_2$ .

\*When these reactions were carried out in the presence of  $\text{Cu}_2\text{Cl}_2$ ;  $\text{CH}_2\text{Cl}_2$  extract was not allowed to expose to air because in the presence of air, the colour of the solution (red-purple) was changed to blue-violet possibly because of the oxidation of cuprous ion.

20 ml diethyl ether was slowly added to the dichloromethane extract whereby red-purple microcrystals of the complex were separated out. These were recrystallised from  $\text{CH}_2\text{Cl}_2$ /diethyl ether.

(i) Preparation of  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\mu\text{-C}_{12}\text{H}_{15}\text{M})\text{L}_4]\text{Y}_2$  ( $\text{L} = \text{PPh}_3$ ,  $\text{AsPh}_3$ ,  $\text{SbPh}_3$ ;  $\text{Y} = \text{HgCl}_3$ ,  $\text{Cu}_2\text{Cl}_2$ ;  $\text{M} = \text{HgCl}$ ,  $\text{CuCl}$ )

The reactions were carried out by a procedure similar to that described in (h) employing  $[(\eta\text{-C}_5\text{H}_5)_2\text{RuL}_2\text{Cl}]$  (0.5 g, ca. 0.67 mmol), (0.4 ml, ca. 0.5 mmol) of  $\text{HC}\equiv\text{C-CMeEtOH}$  and  $\text{HgCl}_2/\text{Cu}_2\text{Cl}_2$  in methanol (40 ml) as reactants. The resulting red purple solution when worked up by the procedure as described in (h), afforded red-purple microcrystals.

These reactions were also repeated by the procedure described in (e) except that the base  $\text{NaOCH}_3$ ,  $\text{KOH/MeOH}$  or  $\text{Na}_2\text{CO}_3$  was used in place of  $\text{NaBH}_4$  or  $\text{LiAlH}_4$ . In every case the corresponding hydrido complex of the type  $(\text{Ru-H})$  was isolated (these complexes have shown strong band in IR at  $1970\text{ cm}^{-1}$  due to  $\text{Ru-H}$ ).<sup>9</sup>

All the above reactions were also carried out in the presence of other anions like  $\text{NaBPh}_4$ ,  $\text{NH}_4\text{PF}_6$  in place of  $\text{NaBF}_4$ .

## Results and Discussion

The complexes formed as a result of the substitution reactions between  $\gamma$ -hydroxyacetylenes and complexes  $[(\eta-C_5H_5)-RuL_2Cl]$  along with their respective empirical formulae derived from the Microanalytical and spectral data are listed in Table VI.1. They have been found to be air stable, highly soluble in solvents like MeOH,  $CH_2Cl_2$ , THF, etc. but insoluble in diethyl ether and hydrocarbons.

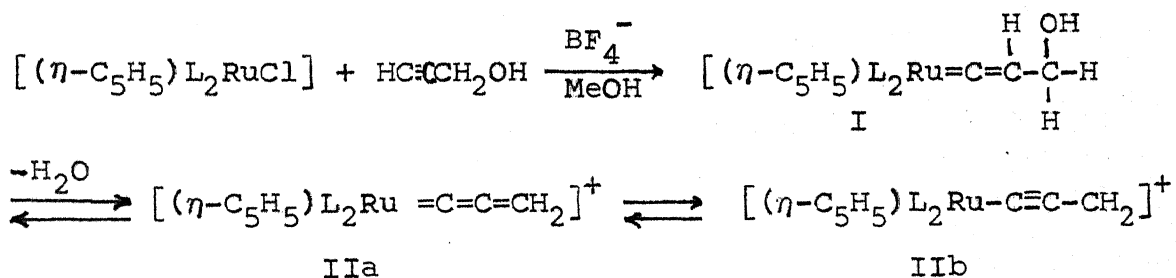
The IR spectra of the complexes (1-7) exhibited strong to medium intensity bands around  $1640\text{ cm}^{-1}$  ( $\nu C=C$ )<sup>2a</sup> and those of allenylidene (8-16), around  $1970\text{ cm}^{-1}$  ( $\nu C=C=C$ )<sup>2a</sup>. Besides the characteristic bands of  $EPh_3$  ( $E = P, As \text{ or } Sb$ ) and  $C_5H_5$  an additional band around  $1622\text{ cm}^{-1}$  (characteristic of phenyl group)<sup>10</sup> was observed in the spectra of complexes containing phenylacetylene and a strong band at  $1050\text{ cm}^{-1}$  (characteristic of  $BF_4^-$  ion)<sup>21</sup> in all of these cationic complexes.

<sup>1</sup>H NMR spectra of the complexes (1-15) exhibited the expected single sharp singlet for the  $C_5H_5$  protons around  $\delta 5.0$  and a broad multiplet in the aromatic region  $\delta (7.0-8.0)$  assigned to  $EPh_3$  and  $C_2Ph$  protons (see Table VI.1). In addition a single sharp peak at  $\delta 5.43$  is assigned to the proton on  $\beta$ -carbon in complexes (1-7). The allenylidene complexes (8-15) showed the absorption at  $\delta 3.3$  for  $CH_2$ <sup>10</sup> (propadienylidene complexes 8-11)



and at  $\delta 0.5-1.8$  for cyclohexane ring protons (complexes 12-15). It appears that the formation of the complexes (1-15) takes place by the heterocyclic dissociation of the highly polarised ruthenium-chloride bond of  $[(\eta-C_5H_5)RuL_2Cl]$ ,<sup>11</sup> followed by the alkyne coordination with a subsequent 1,2-hydrogen shift to form vinylidenes (in case of phenylacetylenes) and hydroxyvinylidenes (in the case of hydroxyacetylenes) complexes (Scheme VI.1). We were able to isolate complexes of the type I (of Scheme VI.1) in very low yield in case of propargyl alcohol.<sup>12</sup> Furthermore, under the reaction conditions complexes of the type I seems to be spontaneously dehydrating to form allenylidene complexes of the type II which are possibly stabilised due to their mesomeric forms IIa and IIb.<sup>3a</sup> (Yield of  $\eta'$ -allenylidene complexes (8-11) is much greater (80%) compared to that of  $\eta'$ -vinylidene ones (4-7), (10%) in the propargyl alcohol reactions.).

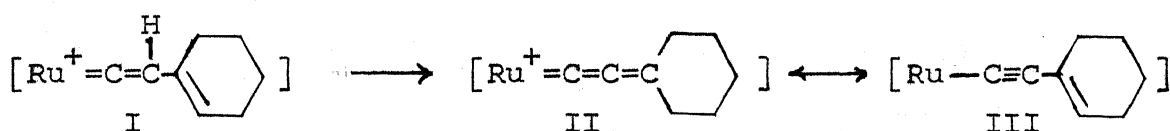
#### Scheme VI.1



In the spectra of ethynylcyclohexanol allenylidene complexes (12-15) two sharp singlets for  $C_5H_5$  protons at  $\delta 5.0$  and

$\delta$  5.05 along with a weak and broad band at  $1565\text{ cm}^{-1}$  besides  $1970\text{ cm}^{-1}$  band in their spectra were also observed. Furthermore the  $^{13}\text{C}$  NMR spectra of these complexes exhibited a number of signals in high field region due to cyclohexane carbons (see Fig. 6.6). One could explain the appearance of these bands in their spectra on the presumption that the following equilibrium exists between the three mesomeric forms similar to that proposed in the structural analyses of  $[(\text{CO})_5\text{Cr}(\eta^1\text{-C}=\text{C}=\text{C}(\text{Ph})(\text{NMe}_2))]^{3a}$  and  $[(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)_2\text{Ru}=\text{C}=\text{C}=\text{CPh}_2]$ .<sup>4</sup>

Scheme VI.2



$(\eta\text{-C}_5\text{H}_5)$ , L groups are omitted in the proposed Scheme.

Such an equilibrium has also been demonstrated by Hoffmann et al. in order to maximise  $\pi$ -orbital overlap in the model compound  $[(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta^1\text{-C}=\text{C}=\text{CH}_2)]^+$ . A substantial contribution from two different mesomeric forms II and III with cationic charge stabilised by both the metal center and the cyclohexane allenylidene (carbenium) moiety is also substantiated by the presence of a large number of peaks in their  $^{13}\text{C}$  and  $^1\text{H}$  NMR (for  $\text{C}_5\text{H}_5$  protons) spectra of their complexes. The metal bonded carbene carbon showed low intensity peak at  $\delta 306\text{ ppm}^{2a}$  for propadienylidene complexes.

Though Selegue has recently reported<sup>14</sup> the formation of a complex of the type I (Scheme VI.2) by the reaction of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PMe}_3)_2\text{Cl}]$  with ethynylcyclohexanol there exists equal possibility for the formation of both the types. We think on the following grounds that the complexes synthesized by us in the case of ethynylcyclohexanol belongs to the type II only. Although the IR spectra of these complexes indicated a very weak band at  $1565\text{ cm}^{-1}$  which could be taken as due to the presence of the type I and which possibly we were not able to isolate, the reaction of the base of form the neutral complexes yielded exclusively  $[\text{Ru}-\text{C}\equiv\text{C}-\overline{\text{C}=\text{C}}-(\text{CH}_2)_4]$  species. Moreover this observation, is further supported by the fact that the formation of  $\eta$ -allenylidene complexes of the type II is not possible by dehydrobromination as a result of reaction of  $\text{HC}\equiv\text{C}-\text{C}_6\text{H}_{10}\text{Br}$  with  $[(\eta\text{-C}_5\text{H}_5)\text{-RuL}_2\text{Cl}]$ , even after refluxing for a few hours though one may expect the formation of  $\eta'$ -vinylidene complexes of the type  $[\text{Ru}^{\text{H}}=\text{C}=\text{C}-\text{C}_6\text{H}_{10}\text{Br})$ . Surprisingly no such product was isolated and in every case the original complexes resulted.

The low field signal (due to  $\alpha$ -carbon) in the  $^{13}\text{C}$  NMR spectra of the  $[\text{Ru}^+=\text{C}=\text{C}=\text{C}_6\text{H}_{10}]$  complexes was not observed. In general, the carbon attached to the metal center absorbs very weakly and the literature reveals that in some of the iron complexes<sup>2d</sup> the  $^{13}\text{C}$  spectra did not exhibit this signal even after 10,000 scans. The spectrum, however, showed  $\beta$ -carbons of the of the vinylidene ligands resonating at  $\delta 120$  ppm and that

of the allenylidene ligands at ca. 191 ppm besides the other characteristic signals due to  $C_5H_5$  and  $EPh_3$  ligands. In the spectrum of the complex 12 two resonances were observed at  $\delta$  90.838 and  $\delta$  90.475 due to  $C_5H_5$  carbons. Besides these, a number of absorption peaks were also observed in  $\delta$  0-60 region while neutral complex 27 showed only four peaks. This behaviour could possibly be explained by assuming an equilibrium between II and III (Scheme VI.2) in solution.

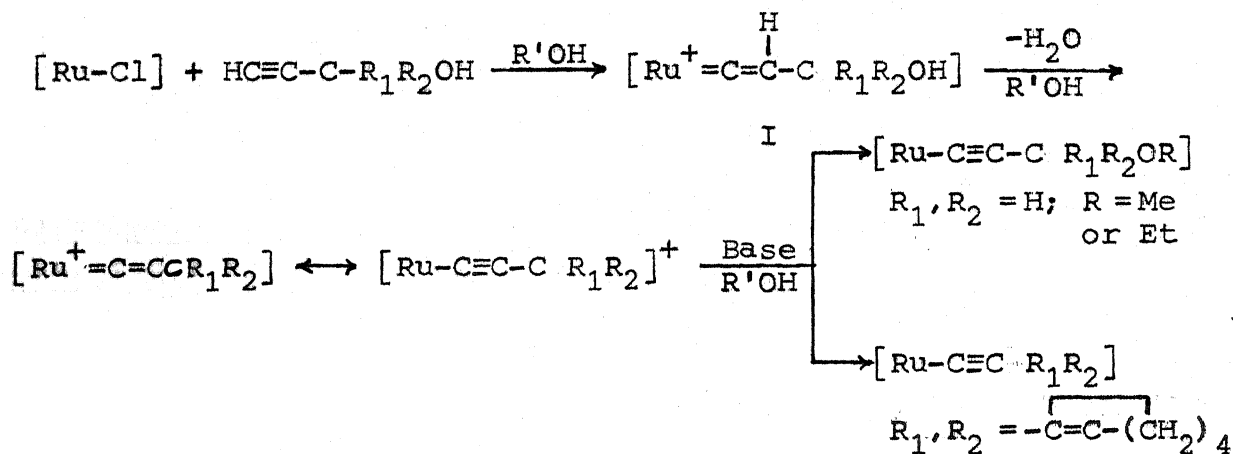
All the cationic complexes (1-15) yielded neutral complexes on treatment with base like  $NaBH_4$ . These were readily characterised by observing a strong  $\nu(C\equiv C)$  band in their IR spectra at  $2080\text{ cm}^{-1}$  and a single sharp peak at  $\delta$  4.1 in their  $^1H$  NMR spectra due to  $C_5H_5$  protons. The high chemical shift of the  $C_5H_5$  protons compared to cationic complexes ( $\delta$  5.0) suggests the high electron density<sup>15</sup> on the metal site in the neutral complexes in which ethynyl ligand which is less effective  $\pi$ -acid compare to vinylidene or allenylidene ligand ( $\pi$ -acid  $\eta^1-C\equiv C-R$  or  $\pi$ -acid  $\eta^1-C\equiv C=CR_2$ ) is bonded to the metal center.<sup>16</sup> The proton NMR spectra of several  $[\eta-C_5H_5)L_2Ru]^+$  derivatives have suggested a direct relationship between the chemical shift of  $C_5H_5$  group and the degree of 'electron richness' at the metal site.<sup>15</sup>

In the case of ethynylcyclohexanol containing complexes dehydration involves either a  $\beta$ -proton or the ring proton. Though  $OMe^-$  group adduct regioselectively takes place at  $C_3$  carbon in alkynyl complexes of propargyl alcohol, but reports

available in literature suggest that the attack of the base can also take place on  $C_1$  carbon. The choice of the site of attack depends upon the nature (hard or soft)<sup>17</sup> of the base. Thus, Berke<sup>17</sup> has reported that in the manganese complexes  $OMe^-$  group attacks on the  $C_1$  carbon and bases like  $PPh_3$ , etc. on  $C_3$  carbon. In the present case the presence of a  $2080\text{ cm}^{-1}$  band and the absence of any band due to  $\nu(C=C)$  in their spectra suggests the formation of  $C\equiv C$  bond which is possible only when the attack of  $OMe^-$  group is on  $C_3$  carbon. One of the many possible explanations for the latter behaviour might be the relatively lesser steric hindrance at the  $C_3$  carbon compared to  $C_1$ . These complexes showed a sharp signal at  $\delta 3.2$  due to the  $OMe^-$  protons in the proton NMR. It was further substantiated by the facts: (i) that the reactions of complexes  $[(\eta-C_5H_5)RuL_2Cl]$  with  $HC\equiv C-CH_2OCH_3$  yielded products identical to ones obtained after reacting cationic complexes with  $OMe^-$ , and (ii) that using ethanol as the reaction medium in the case of  $HC\equiv C-CH_2OH$  yielded the corresponding  $OEt^-$  group adduct whereas in that of ethynylcyclohexanol, dehydration occurs using ring proton with the formation of a double bond in the ring  $[Ru-C\equiv C-\text{cyclohexyl}]$ .<sup>14</sup> In cationic complexes 12-15 dehydration could take place by the possible routes. (a) Formation of  $\eta'$ -allenylidene (Scheme VI.2); (b) Formation of  $\eta'$ -vinylidene I (Scheme VI.2). In the presence of  $NaBH_4$ , we are able to isolate  $\eta'$ -alkyne complexes having double bond in cyclohexane ring. Similar conclusions were

reached in the reaction of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PMe}_3)_2\text{Cl}]$  with ethynyl cyclohexanol in the presence of base.<sup>14</sup> We, therefore, propose that the formation of all the above neutral complexes take place in accordance with Scheme VI.3 already proposed by others.

Scheme VI.3



$\eta\text{-C}_5\text{H}_5$ , L groups are omitted in proposed scheme

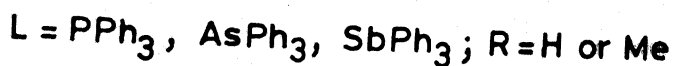
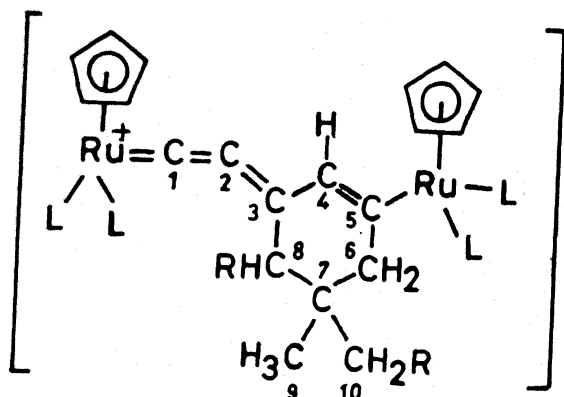
Although a number of bases ( $\text{NEt}_3$ ,  $\text{NaOMe}$  etc.) have been used in the literature to isolate neutral complexes from the cationic one, we were able to synthesize neutral complexes only in the presence of  $\text{NaBH}_4$ . In the presence of  $\text{NaOMe}$ , the reaction yielded hydrido complexes ( $\text{Ru-H}$ ).<sup>9</sup>

The  $^{13}\text{C}$  NMR spectra of the complexes (19, 27, 28) exhibited several resonances assigned to the carbons of  $\text{C}_5\text{H}_5$ , and  $\eta'$ -alkyne ligand. In the spectrum of complex 19 no signals was observed in the high field whereas in that of the complex 27, only four signals were observed attributed to the cyclohexene

ring compared to several peaks in its corresponding cationic complexes as stated before also. The difference in the spectra of the latter complex could be explained either by the rapid (on  $^{13}\text{C}$  NMR scale) free rotation of allenylidene ligand moiety with respect to the  $[(\eta\text{-C}_5\text{H}_5)\text{RuL}_2]$  symmetry plane at room temperature or the formation of the mesomeric cations (II and III in Schemes VI.1 and VI.2) is not possible in solution, similar to the corresponding cationic complexes at room temperature.

#### Diruthenium Allenylidene - vinyl and Vinylidene alkylidene Complexes

The deep blue allenylidene complexes were synthesized by refluxing parent chlorides with substituted propargyl alcohols, viz., 3-methyl-3-hydroxybuta-1-yne and 3-methyl-3-hydroxypenta-1-yne in methanol. Though Selegue<sup>5</sup> for the first time reported the formation of vinylidene-alkynyl complex by stirring the triphenylphosphine complex with substituted propargynol ( $\text{HC}\equiv\text{C-CMe}_2\text{OH}$ ) in methanol for 21 hr. We were able to isolate them within 20 minutes. Table VI.2 indicates the IR,  $^1\text{H}$  NMR and other spectral properties of these complexes. These complexes were found to be similar in their chemical behaviour to those of the reported one and, therefore, were assumed to be dimers of the expected dialkyl-allenylidene complex  $[\text{Ru}=\text{C}=\text{C}=\text{C}(\text{Me})\text{R}]$  ( $\text{R} = \text{Me, Et}$ ). The central proton of the cation is illustrated below:



Two typical  $[(\eta-C_5H_5)RuL_2]^{18}$  moieties are bonded to a bridging  $\mu-C_nH_m$  ( $n = 10 \text{ or } 11; m = 12 \text{ or } 16$ ) ligand resulting from the formation of two carbon-carbon bonds ( $C_4-C_5$  and  $C_7-C_8$ ) between two  $C=C=CMeR$  ( $R = Me \text{ or } Et$ ) moieties with simultaneous migration of two protons. The  $Ru_1-C_2-C_3$  group comprises an allenylidene linkage as suggested by IR spectroscopy exhibiting a band at  $1970 \text{ cm}^{-1}$  due to asymmetric  $\nu_{asym}(C=C=C)^{2a}$  and the second ruthenium atom is bonded to the cyclohexene ring by an vinylidene carbon bond between  $Ru_2$  and  $C_5$  similar to the one described by Selegue in his paper.

The deep blue solutions of allenylidene-vinyl complexes in organic solvents ( $\lambda_{max}$ : 575 nm) which are stable for several days, became deep red-purple ( $\lambda_{max}$ : 500 nm) in the presence of strong acids like  $HClO_4$  or  $CF_3COOH$  and the latter solutions are highly sensitive towards atmospheric moisture to give back to the parent blue complexes. The dicationic red-purple coloured vinylidene-alkylidene complexes were formed by protonating the



$\beta$ -carbons ( $C_2$ ) in blue complexes which can be readily deprotonated using any base like  $NEt_3$  or  $NH_4OH$ .

Interestingly the reactions carried out between  $[(\eta-C_5H_5)-RuL_2Cl]$  and  $HC\equiv C-CMe(R)OH$  ( $R = Me$  or  $Et$ ) in the presence of  $HgCl_2$  or  $Cu_2Cl_2$  yielded red-purple vinylidene-alkylidene complexes containing  $Hg(II)$  or  $Cu^{1+}$  which were found to be air stable. Even the solutions of these complexes were stable to atmospheric moisture (except  $Cu_2Cl_2$  complexes). Preliminary studies indicated that possibly highly labile vinyl proton ( $\beta$ -carbon) was substituted by one molecule of  $HgCl^+$  or  $Cu_2Cl^+$  forming some sort of a metal complex having  $C_2-HgCl$ ,<sup>19</sup> or  $C_2-Cu_2Cl$  bond.<sup>20</sup> This bond is found to be stronger in mercury complex compared to that in copper complex (because of this reason the reactions of  $CuCl$  carried out in dry methanol under inert gas atmosphere). The red-purple complexes exhibited a band at  $1565\text{ cm}^{-1}$  assigned to  $\nu(C=C)$  in their IR and two sharp resonances for  $C_5H_5$  protons at  $\delta$  5.55 and 4.9 ppm besides other characteristic signals for  $C_6H_5$ ,  $CH_3$  and  $CH_2$  in their  $^1H$  NMR spectra.

In the presence of strong base like  $NMe_3$  or  $NH_4OH$  these were converted to allenylidene-vinyl complexes which in the presence of strong acid like  $HClO_4$  changed to vinylidene-alkylidene complexes by substituting  $HgCl_2$  with the proton on  $\beta$ -carbon.

The  $^{13}C$  NMR spectrum of complex 31 ( $\delta$  C 277.2 ( $C_1$ ), 198.39 ( $C_2$ ), 142.43 ( $C_3$ ), 140.36 ( $C_4$ ), 151.55 ( $C_5$ ), 127.36-137.6 (Ph),

90.7 and 87.67 ( $CP_1$  and  $CP_2$ ) and 27 to 68 for cyclohexane ring carbons) clearly shows the presence of an unsaturated alkylidene ligand. The shift of  $C_5H_5$  carbons towards high field side is in accordance with the high field shift of  $C_5H_5$  protons in proton NMR spectrum because of the high 'electron richness' at the metal centers due to high conjugation of  $[Ru=C=C-C-C-C-Ru]$  system.<sup>16</sup> The increased conjugation in the blue complexes is further demonstrated by the shift in the position  $\lambda_{max}$  in their electronic spectra towards low energy side (575 or 500 nm) compared to that in the tan-coloured complexes ( $\lambda_{max}$ : 375-525 nm). It is further speculated that there should be some relationship between the chemical shift of the  $C_5H_5$  carbons or protons and the degree of electron density on metal site.<sup>15</sup>

The formation of all these complexes with (i) propargyl alcohols, (ii) substituted propargyl alcohol, (iii) ethynyl-cyclohexanol, (iv) their neutral complexes suggest that the formation of these complexes undoubtedly proceeds via the dehydration of a hydroxy vinylidene intermediate. In the case of blue or red-purple complexes vinylidene intermediate plays a role in the dimerization of  $[(\eta-C_5H_5)L_2Ru(C=C-CMe(R))]^+$ .

TABLE

$[\text{Ru}]^+ = \text{C}=\text{C}-\text{R}$ $\text{H}$ $ $	$[\text{Ru}]^+ = \text{C}=\text{C} \text{ RR}_1$				$[\text{Ru}]-\text{C}\equiv\text{C}-\text{R}$				$[\text{Ru}]^+ = \text{C}=\text{C}$ $\text{H}$ $ $ $\text{RHC}$ $\text{H}_3\text{C}$ $\text{R}_1$				$[\text{Ru}]^+ = \text{C}=\text{C}$ $\text{M}'$ $ $ $\text{RHC}$ $\text{H}_3\text{C}$ $\text{R}_1$ $\text{M}' = \text{HgCl}$							
Com- pound No.	E	E'	R	Com- pound No.	E	E'	R	Com- pound No.	E	E'	R	Com- pound No.	E	E'	R	Com- pound No.	E	E'	R	R <sub>1</sub>
1	As	P	Ph	8	P	P	H	16	As	P	Ph	31	P	P	H	Me	P	P	H	Me
2	As	As	Ph	9	P	As	H	17	As	As	Ph	32	As	P	H	Me	As	P	H	Me
3	Sb	Sb	Ph	10	As	As	H	18	Sb	Sb	Ph	33	As	As	H	Me	As	As	H	Me
4	P	P	CH <sub>2</sub> OH	11	Sb	Sb	H	19	P	P	CH <sub>2</sub> OMe	34	Sb	Sb	H	Me	Sb	Sb	H	Me
5	As	P	CH <sub>2</sub> OH	12	P	P	-(CH <sub>2</sub> ) <sub>5</sub> -	20	As	P	CH <sub>2</sub> OMe	35	P	P	Me	Et	P	P	Me	Et
6	As	As	CH <sub>2</sub> OH	13	P	As	-(CH <sub>2</sub> ) <sub>5</sub> -	21	As	As	CH <sub>2</sub> OMe	36	As	P	Me	Et	As	P	Me	Et
7	Sb	Sb	CH <sub>2</sub> OH	14	As	As	-(CH <sub>2</sub> ) <sub>5</sub> -	22	Sb	Sb	CH <sub>2</sub> OMe	37	As	As	Me	Et	As	As	Me	Et
				15	Sb	Sb	-(CH <sub>2</sub> ) <sub>5</sub> -	23	P	P	CH <sub>2</sub> OEt	38	Sb	Sb	Me	Et	Sb	Sb	Me	Et
								24	As	P	CH <sub>2</sub> OEt									
								25	As	As	CH <sub>2</sub> OEt									
								26	Sb	Sb	CH <sub>2</sub> OEt									
								27	P	P	$-\text{C}=\text{C}(\text{CH}_2)_4$									
								28	P	As	$-\text{C}=\text{C}(\text{CH}_2)_4$									
								29	As	As	$-\text{C}=\text{C}(\text{CH}_2)_4$									
								30	Sb	Sb	$-\text{C}=\text{C}(\text{CH}_2)_4$									

$[\text{Ru}]^+ = [\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{EPPh}_3)(\text{E}'\text{Ph}_3)]$

$$[\text{Ru}]^+ = [\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{EPH}_3)(\text{E}'\text{Ph}_3)]$$

Table VI.1 Analytical and Physical Data for  $\eta^1$ -Vinylidene,  $\eta^1$ -allenylidene and  $\eta^1$ -alkynyl complexes

a colour	b M.P. °C	Found (Calc.) %		IR of C=C (asym)(cm <sup>-1</sup> )	<sup>1</sup> H NMR δ(ppm)C					<sup>13</sup> C NMR (δppm)						
		C	H		Cp	CH <sub>2</sub>	= CH	OH	Cp	Ph	N=C	C=C	=C R	Others		
2	3	4	5	6	7	8	9	10	11	12	13	14	15	16		
T.P.	110	63.15 (63.7)	4.8 (4.4)	1640	5.93	-	5.3t									
T.P.	110	60.2 (60.8)	4.7 (4.2)	1640	5.35	-	5.6t	-	90.76	127.0- 134.24	-	-	94.78	88.72		
T.P.	112	55.2 (55.4)	4.2 (3.8)	1645	4.95	-	5.2t	-								
m	145	62.8 (63.4)	5.7 (4.8)	1610	5.04	3.2	5.21	2.02	90.74	127.0- 134.17	306	-	94.7 94.5			
m	145	60.5 (60.2)	5.4 (4.4)	1610	5.0	3.2	5.23	2.01								
m	146	57.0 (57.3)	4.7 (4.2)	1615	4.93	3.2	5.16	2.02								
m	149	51.9 (52.1)	4.3 (3.8)	1615	5.2	3.3	5.2	2.02								
y	150	64.3 (64.7)	5.2 (4.57)	1960	5.0	3.5	-	-	90.79	127.22- 134.85	-	202.87	94.6	93.67, 91.74, 91.36		
														155		

Table VI.1 (contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
9	y	150	60.9 (61.5)	5.1 (4.3)	1960	5.0	3.35	-	-	-	-	-	-	-	-
10	y	149	58.7 (58.5)	5.0 (4.1)	1960	5.1	3.55	-	-	-	-	-	-	-	-
11	y	151	52.9 (52.6)	4.5 (3.7)	1965	5.2	3.4	-	-	-	-	-	-	-	-
12	y	150	67.4 (66.6)	4.7 (5.3)	1970	5.0	1.5 <sup>d</sup>	-	-	93.09	127.32 - 134.02	-	191.22	-	17.55 - 51.73
13	y	149	64.5 (63.4)	4.6 (5.0)	1970	5.0	1.5 <sup>d</sup>	-	-	93.16	128.79 - 133.89	-	191.28	84.15	17.61 - 51.79
14	y	150	60.2 (60.5)	5.2 (4.7)	1970	5.1	1.5 <sup>d</sup>	-	-	-	-	-	-	-	-
15	y	151	54.5 (55.2)	4.5 (4.3)	1960	5.2	1.5 <sup>d</sup>	-	-	-	-	-	-	-	-
16	y	204	69.8 (70.4)	5.2 (4.8)	2085	4.2	-	-	-	-	-	-	-	-	-
17	y	205	66.2 (66.9)	5.0 (4.6)	2085	4.2	-	-	-	-	-	-	-	-	-
18	y	205	59.8 (60.3)	4.7 (4.1)	2085	4.2	-	-	-	-	-	-	-	-	-

Table VI.1 (contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
19	y	183	71.0 (71.4)	5.6 (5.3)	2090	4.0	4.3	-	3.2 ( $\delta\text{CH}_3$ )	81.27	127.01- 133.7	-	138.02- 138.72	-	-
20	y	184	67.1 (67.5)	5.4 (5.0)	2090	4.0	4.3	-	3.2 ( $\delta\text{CH}_3$ )						
21	y	185	63.7 (64.0)	4.5 (4.7)	2090	4.1	4.3	-	3.2 ( $\delta\text{CH}_3$ )						
22	y	185	57.3 (57.2)	4.7 (4.2)	2090	4.2	4.35	-	3.3 ( $\delta\text{CH}_3$ )						
23	y	160	71.0 (71.6)	5.7 (5.41)	2080	4.1	4.3	-	1.6 ( $\delta\text{CH}_3$ )						
24	y	162	67.3 (67.8)	5.5 (5.1)	2080	4.1	4.3	-	1.6 ( $\delta\text{CH}_3$ )						
25	y	161	63.9 (64.3)	5.6 (5.0)	2080	4.1	4.3	-	1.6 ( $\delta\text{CH}_3$ )						
26	y	165	57.4 (57.6)	4.9 (4.4)	2080	4.1	4.3	-	1.6 ( $\delta\text{CH}_3$ )						

Table VI.1 (contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
27	y	185	75.2 (75.7)	5.6 (6.0)	2090	4.2	1.6 <sup>d</sup>	-	-	85.01	124.1- 134.1	-	139.24- 139.94	-	22.55, 23. 21.74, 21.
28	y	184	69.4 (69.8)	5.9 (5.6)	2080	4.2	1.55 <sup>d</sup>	-	-	85.01	127.0- 133.86	-	133.93	-	22.51, 23. 25.73, 51.
29	y	186	67.1 (66.4)	5.7 (5.3)	2080	4.2	1.5 <sup>d</sup>	-	-	-	-	-	-	-	-
30	y	186	60.2 (60.0)	5.2 (4.8)	2080	4.2	1.5 <sup>d</sup>	-	-	-	-	-	-	-	-

a. TP = Tan powder; y = yellow, M = Maroon

b. Melting points are uncorrected

c. Solvents CDCl<sub>3</sub>. Aromatic protons of other colligands appeared in the region  $\delta$  7.0 - 8.0 as broad multiplets

d. Centre of a broad unresolved multiplet

m. multiplet, t = triplet.

Table VI.2. Spectral and analytical data for dimeric complexes

Compound No.	a colour	b M.P.(°C)	Analyses found(Calc.%)	IR band C=C-C (asym)cm <sup>-1</sup>	<sup>1</sup> H NMR (δ ppm) <sup>d</sup>							<sup>13</sup> C NMR (δ ppm)				λ <sub>max</sub> . nm (in CHCl <sub>3</sub> )
					C	H	C <sup>1</sup> <sub>5</sub> H <sup>1</sup> <sub>5</sub>	C <sup>2</sup> <sub>5</sub> H <sup>2</sup> <sub>5</sub>	CH <sub>3</sub>	CH <sub>2</sub>	CH <sub>2</sub> <sup>1</sup>	=CH	C <sup>1</sup> <sub>5</sub> H <sup>1</sup> <sub>5</sub>	C <sup>2</sup> <sub>5</sub> H <sup>2</sup> <sub>5</sub>	Ru=C	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	
31	B	155	68.4 (69.1)	6.1 (5.0)	1770	4.7	4.45	0.7	3.0	1.3	5.0	90.71	87.67	277.27	575	
32	B	154	65.2 (65.4)	5.4 (4.8)	1770	4.7	4.45	0.8	3.0	1.3	5.0	-	-	-	575	
33	B	150-2	61.9 (62.2)	5.3 (4.5)	1770	4.7	4.45	0.8	3.0	1.3	5.0	-	-	-	575	
34	B	146	55.8 (56.2)	3.7 (4.1)	1770	4.7	4.45	0.8	3.0	1.3	5.0 <sub>m</sub>	-	-	-	575	
35	B	125-8	69.7 (69.4)	5.8 (5.2)	1770	4.55	4.43	0.5	← - - - - -> 1.6	5.0 <sub>m</sub>	5.0 <sub>m</sub>	90.76	90.59	277.56	575	
36	B	125-8	64.5 (65.8)	4.5 (5.0)	1770	4.75	4.43	0.5	← - - - - -> 1.6	5.0 <sub>m</sub>	5.0 <sub>m</sub>	-	-	-	575	
37	B	125-8	62.9 (62.6)	5.4 (4.7)	1770	4.6	4.45	0.5	← - - - - -> 1.6	5.0 <sub>m</sub>	5.0 <sub>m</sub>	-	-	-	575	
38	B	125-8	55.7 (56.6)	4.5 (4.3)	1770	4.54	4.42	0.5	← - - - - -> 1.6	5.0 <sub>m</sub>	5.0 <sub>m</sub>	90.85	90.69	-	575	
39	RP	95	45.9 (46.5)	4.0 (3.4)	1565	5.63	5.07	0.8	3.67	1.5	-	-	-	-	498	



Table VI.2 (contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
40	RP	97	44.1 (44.8)	4.5 (3.3)	1565	5.6	5.05	0.8	3.6	1.5	-	-	-	-	498
41	RP	100	42.7 (43.3)	3.0 (3.2)	1565	5.64	5.07	0.5	3.5	1.6	-	-	-	-	500
42	RP	100	40.8 (41.7)	4.0 (3.0)	1565	5.65	5.05	4.5	3.4	1.5	-	-	-	-	500
43	RP	98.100	47.3 (47.0)	4.1 (3.5)	1560	5.4	5.0	0.5	←---→	1.8	-	-	-	-	500
44	RP	105	45.5 (45.30)	3.7 (3.4)	1565	5.5	5.0	0.5	←---→	2.0	-	-	-	-	500
45	RP	104.7	43.1 (43.7)	4.1 (3.3)	1565	5.5	5.0	0.5	←---→	2.0	-	-	-	-	500
46	RP	105.8	42.6 (42.2)	3.6 (3.2)	1565	5.5	5.0	0.5	←---→	2.0	-	-	-	-	500

a. B = Blue, RP = red-purple

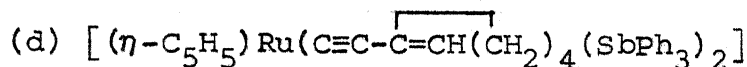
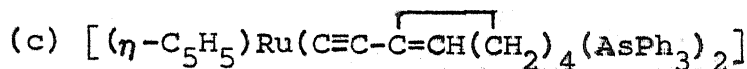
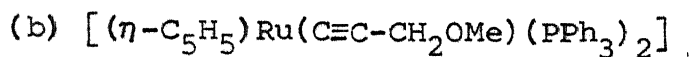
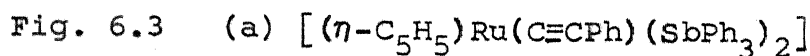
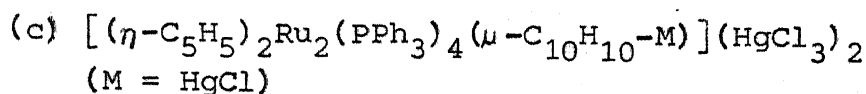
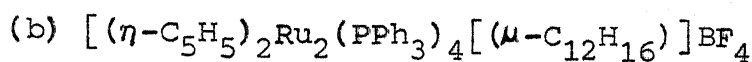
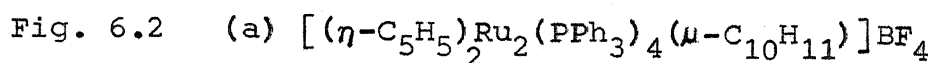
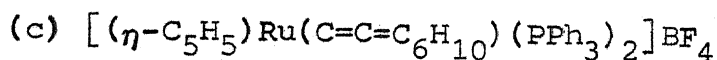
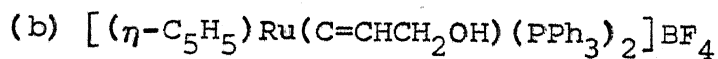
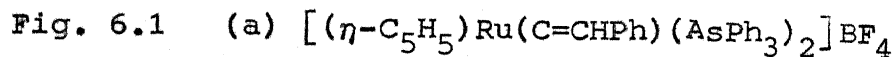
b. Missing points are uncorrected

c. K Br pellets

d. In  $\text{CdCl}_2$  with TIS as internal standard

m = multiplets

## IR SPECTRA OF THE COMPLEXES



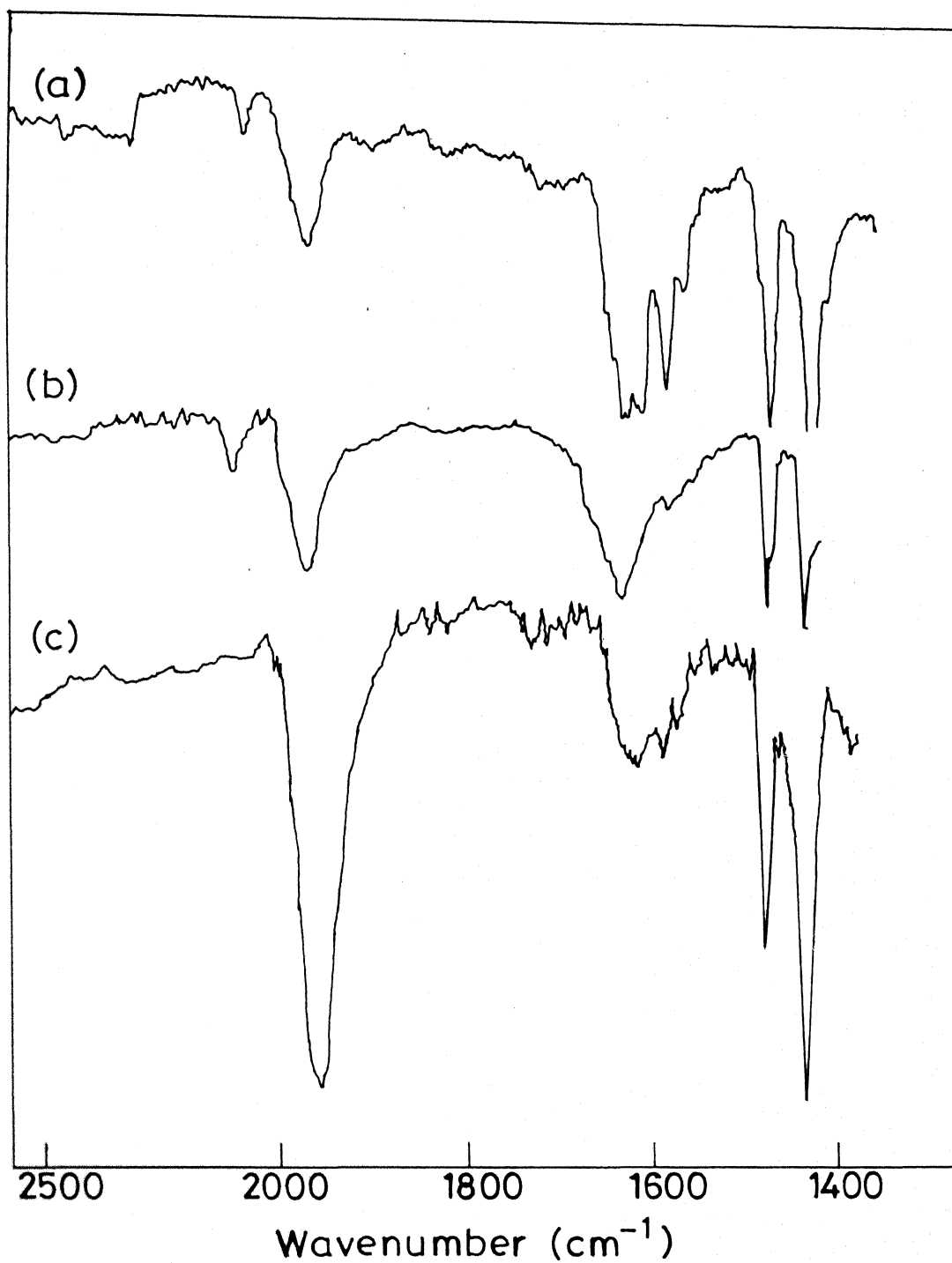


Fig. 6.1 IR spectra of the complexes.

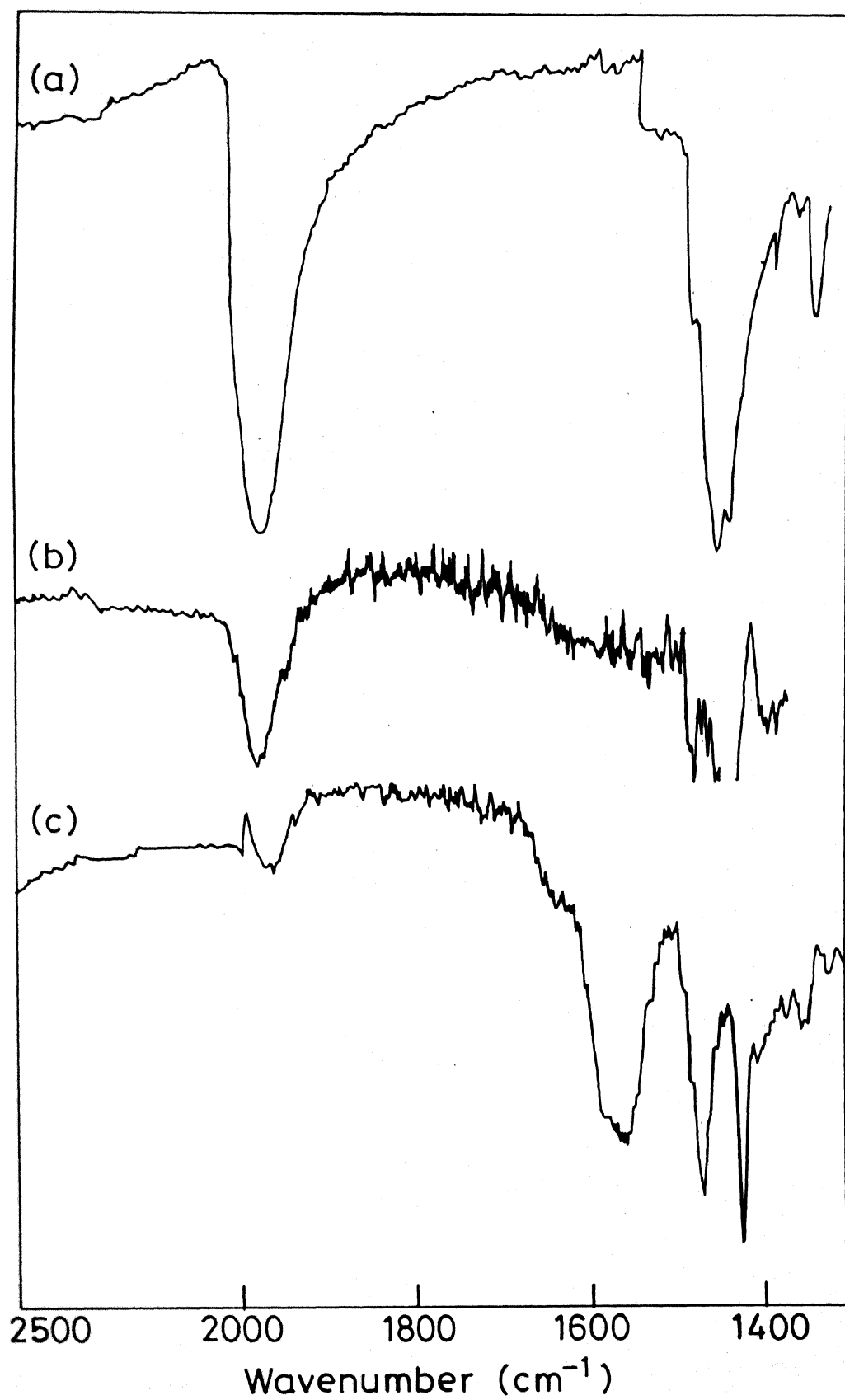


Fig.6.2 IR spectra of the complexes.

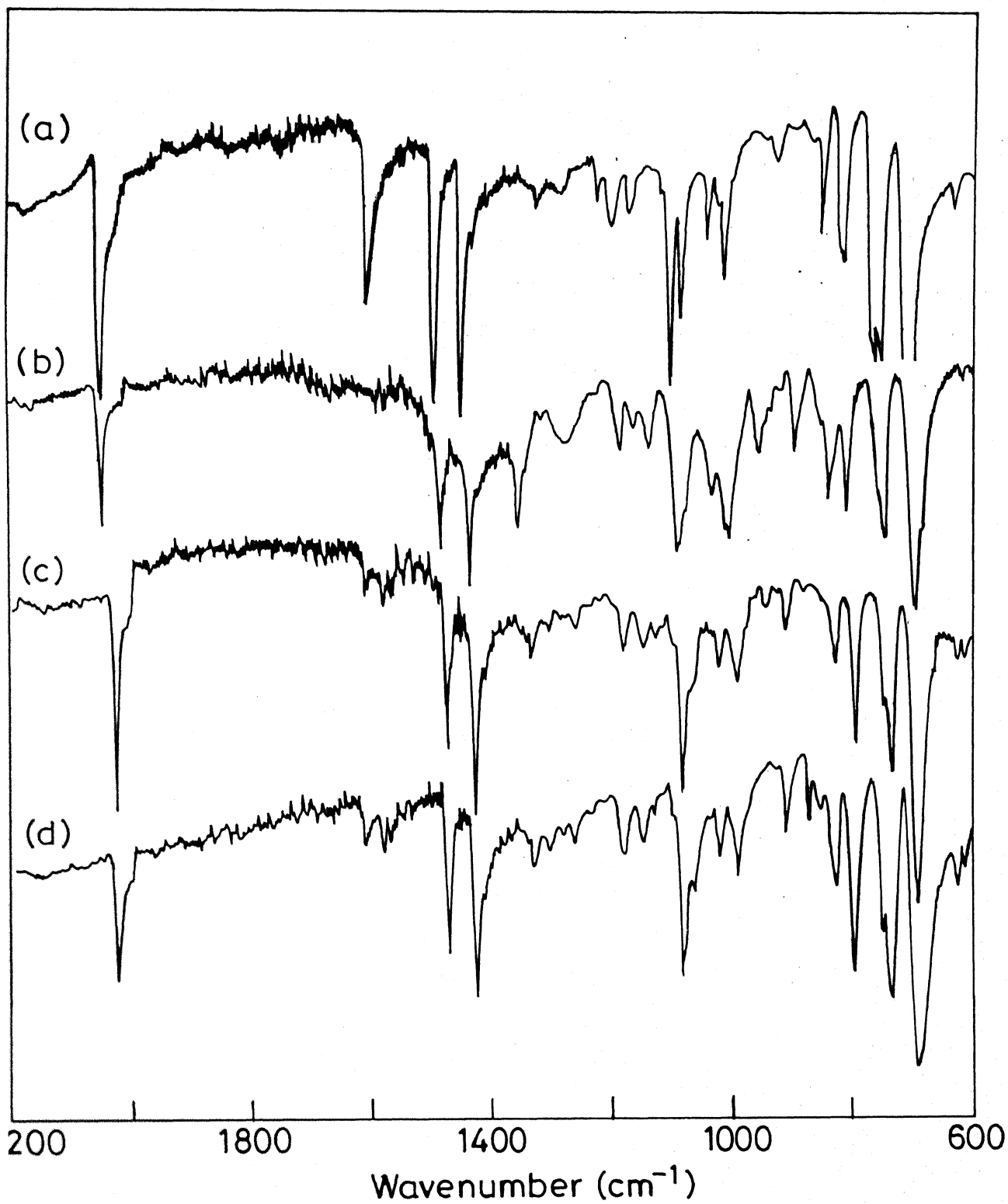
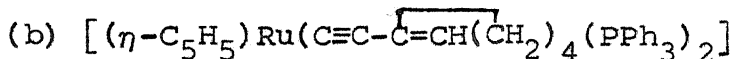
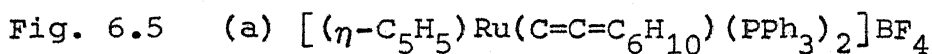
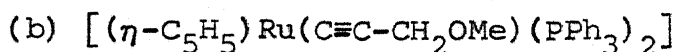
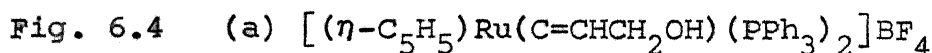
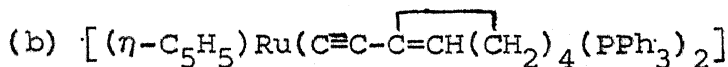
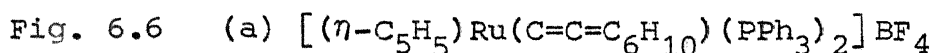
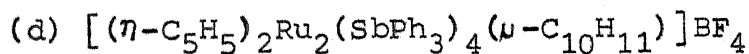
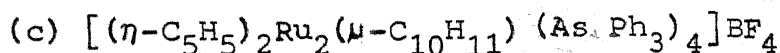
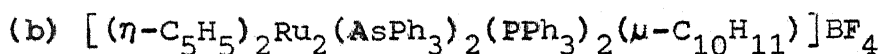
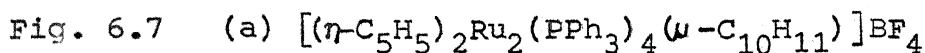


Fig. 6.3 IR spectra of the complexes.

<sup>1</sup>H NMR SPECTRA OF THE COMPLEXES<sup>13</sup>C NMR SPECTRA OF THE COMPLEXES<sup>1</sup>H NMR SPECTRA OF THE COMPLEXES

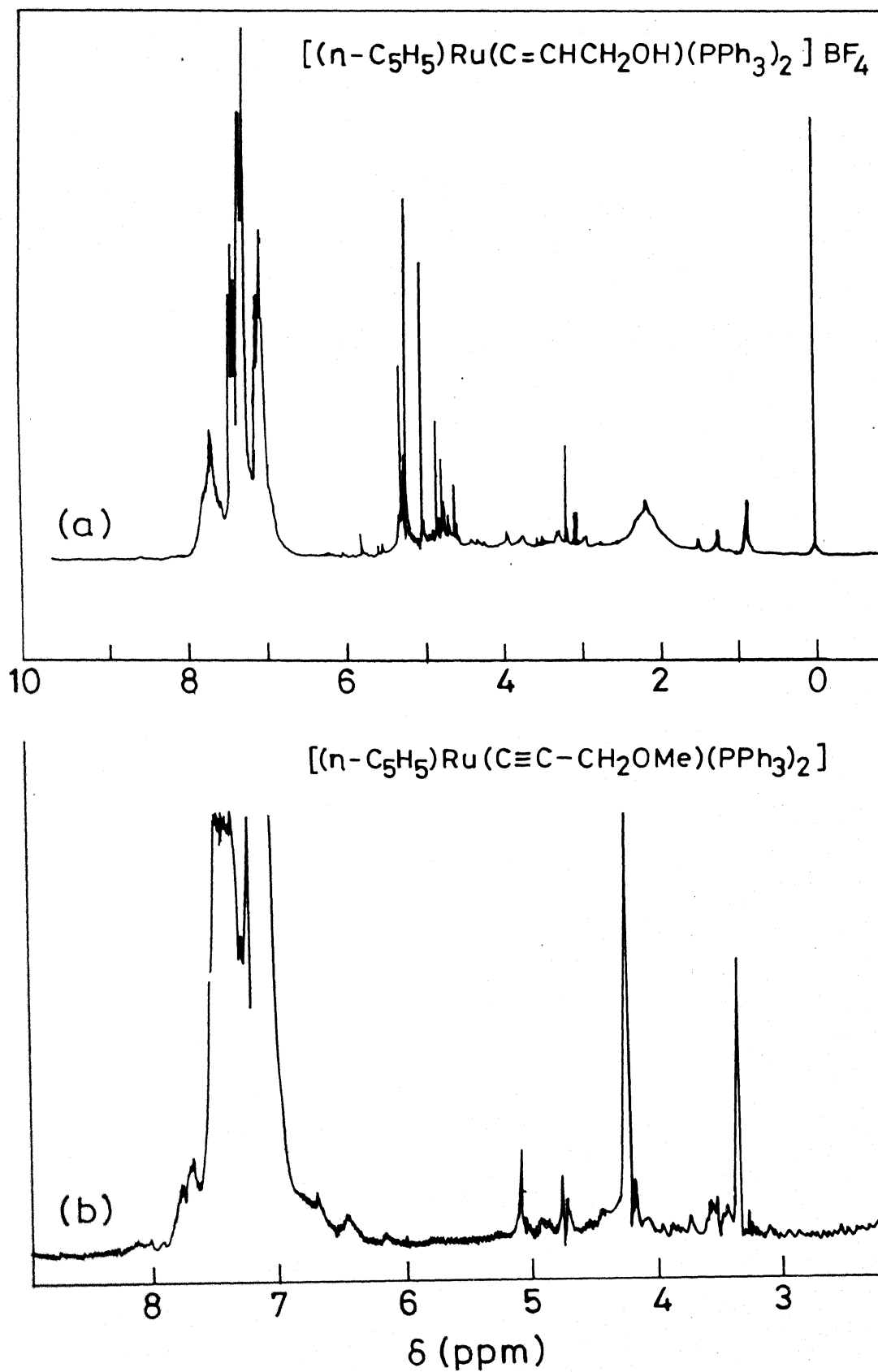
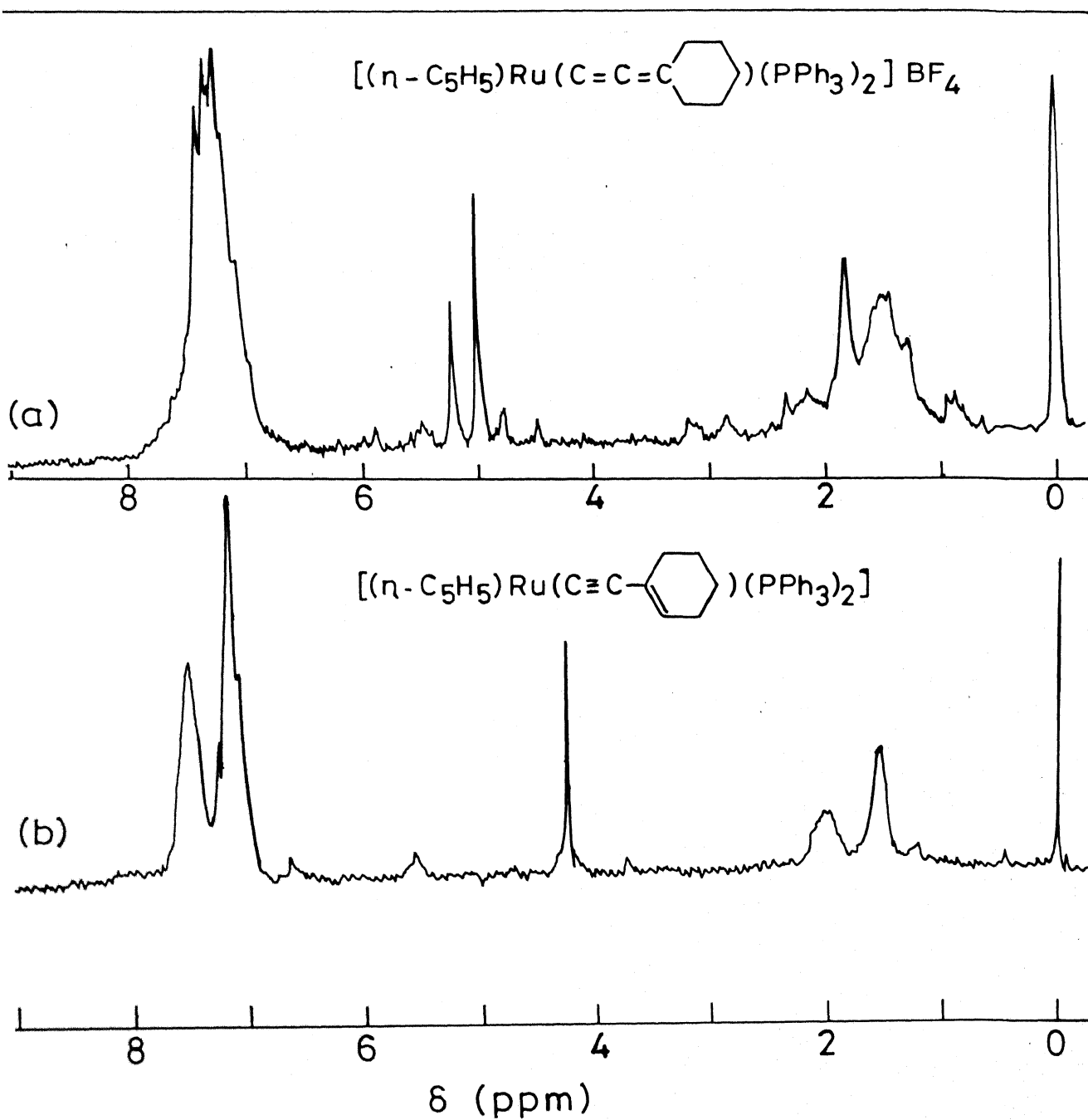


Fig. 6.4  $^1\text{H}$  NMR spectra.

Fig. 6.5  $^1\text{H}$  NMR spectra.



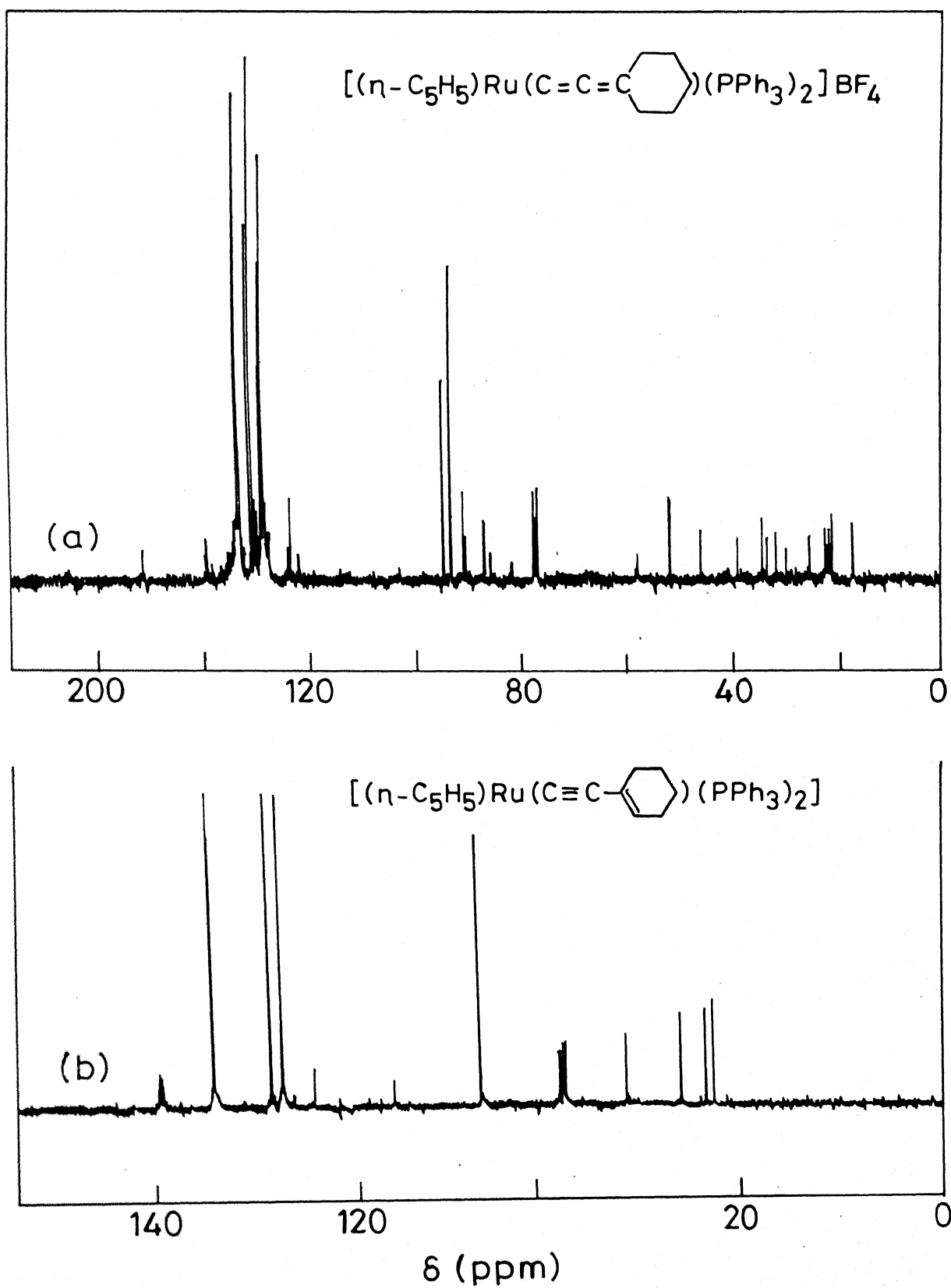


Fig.6.6  $^{13}\text{C}$  NMR spectra.

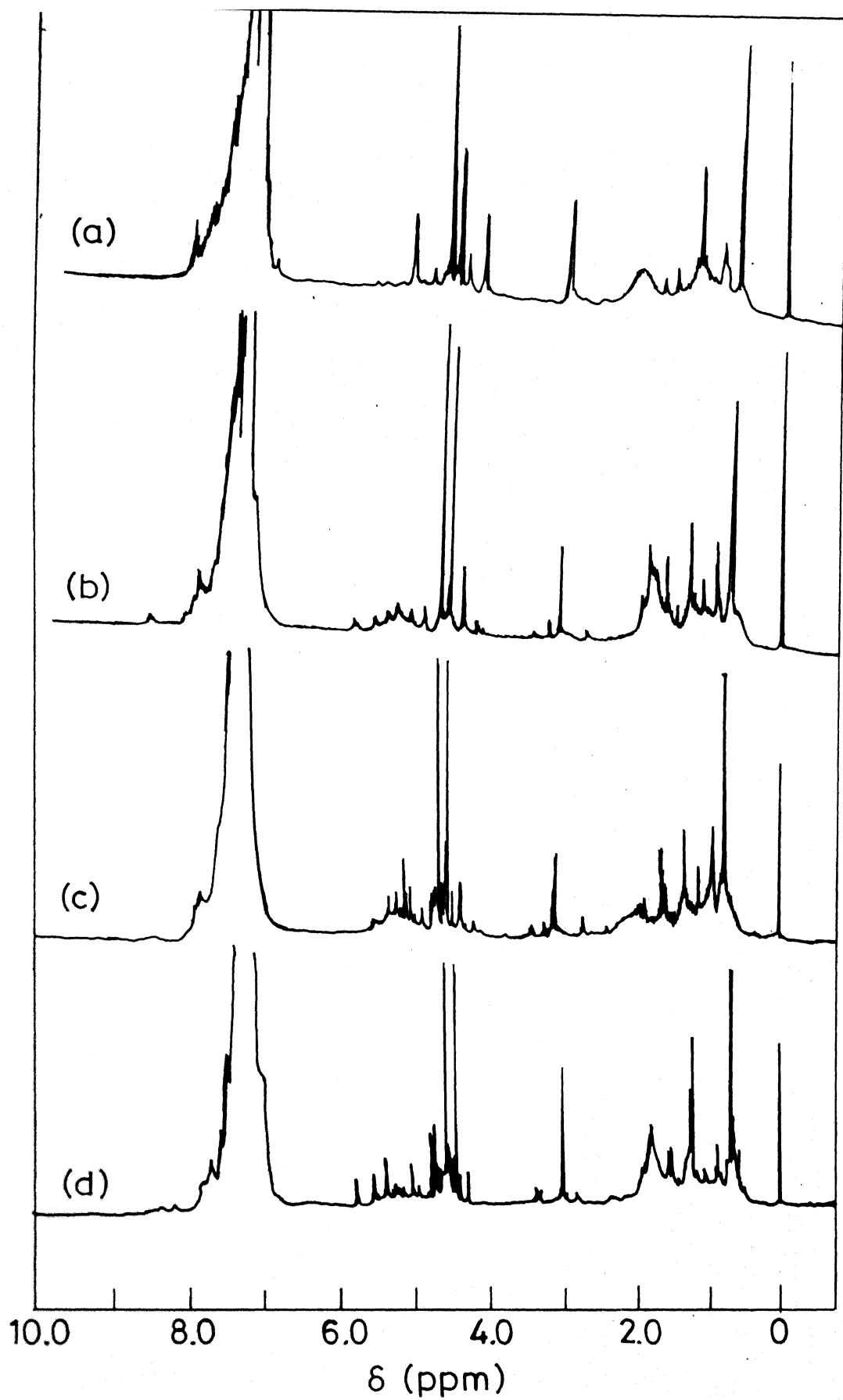


Fig. 6.7  $^1\text{H}$  NMR spectra.

<sup>1</sup>H NMR SPECTRA OF THE COMPLEXES

Fig. 6.8  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{AsPh}_3)_4(\mu\text{-C}_{12}\text{H}_{16})]\text{BF}_4$

Fig. 6.9a  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{PPh}_3)_4(\mu\text{-C}_{12}\text{H}_{16})]\text{BF}_4$

b  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{SbPh}_3)_4(\mu\text{-C}_{12}\text{H}_{16})]\text{BF}_4$

<sup>13</sup>C NMR SPECTRUM OF THE COMPLEX

Fig. 6.10  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{PPh}_3)_4(\mu\text{-C}_{10}\text{H}_{11})]\text{BF}_4$

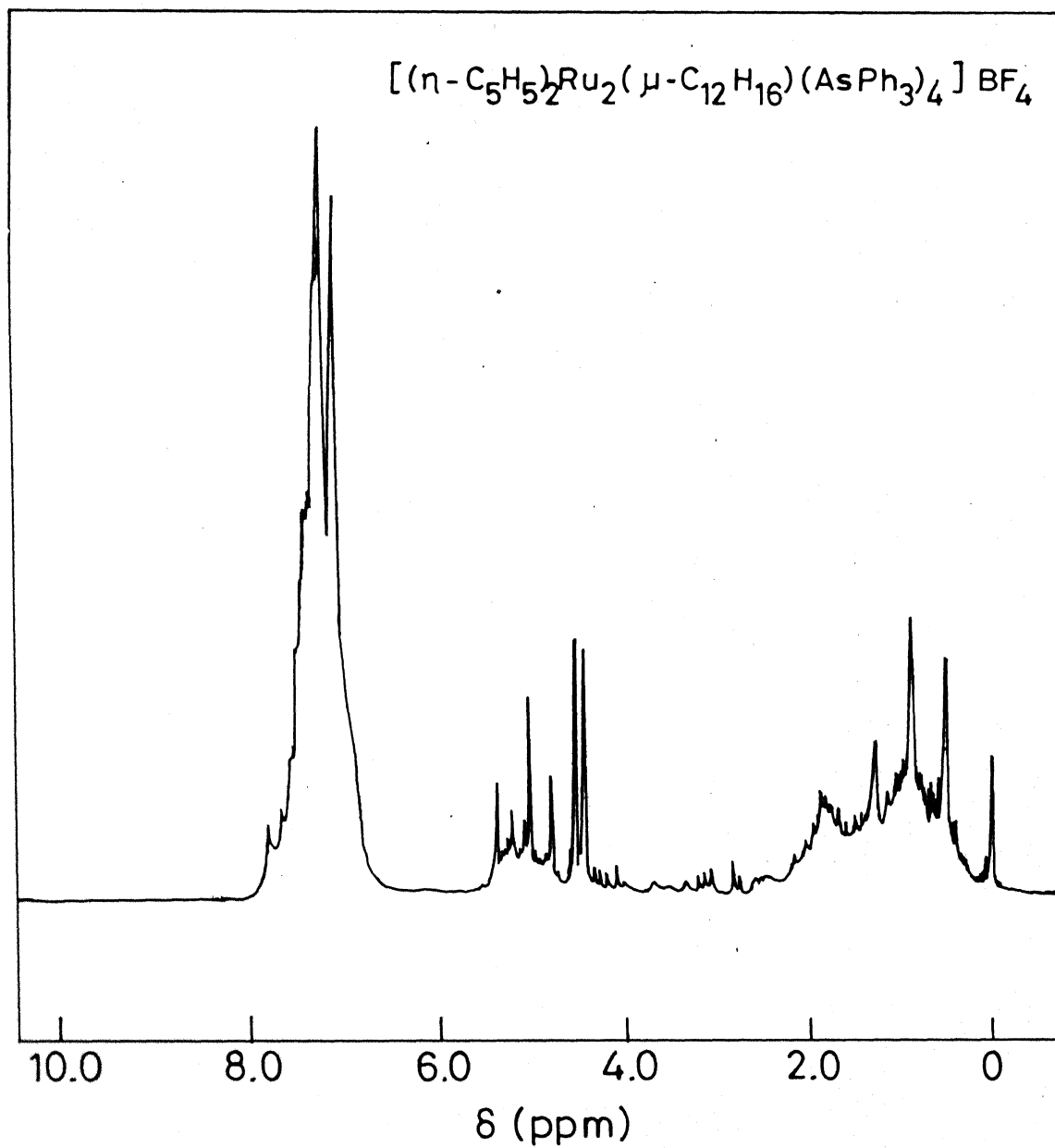


Fig. 6.8  $^1H$  NMR spectrum.

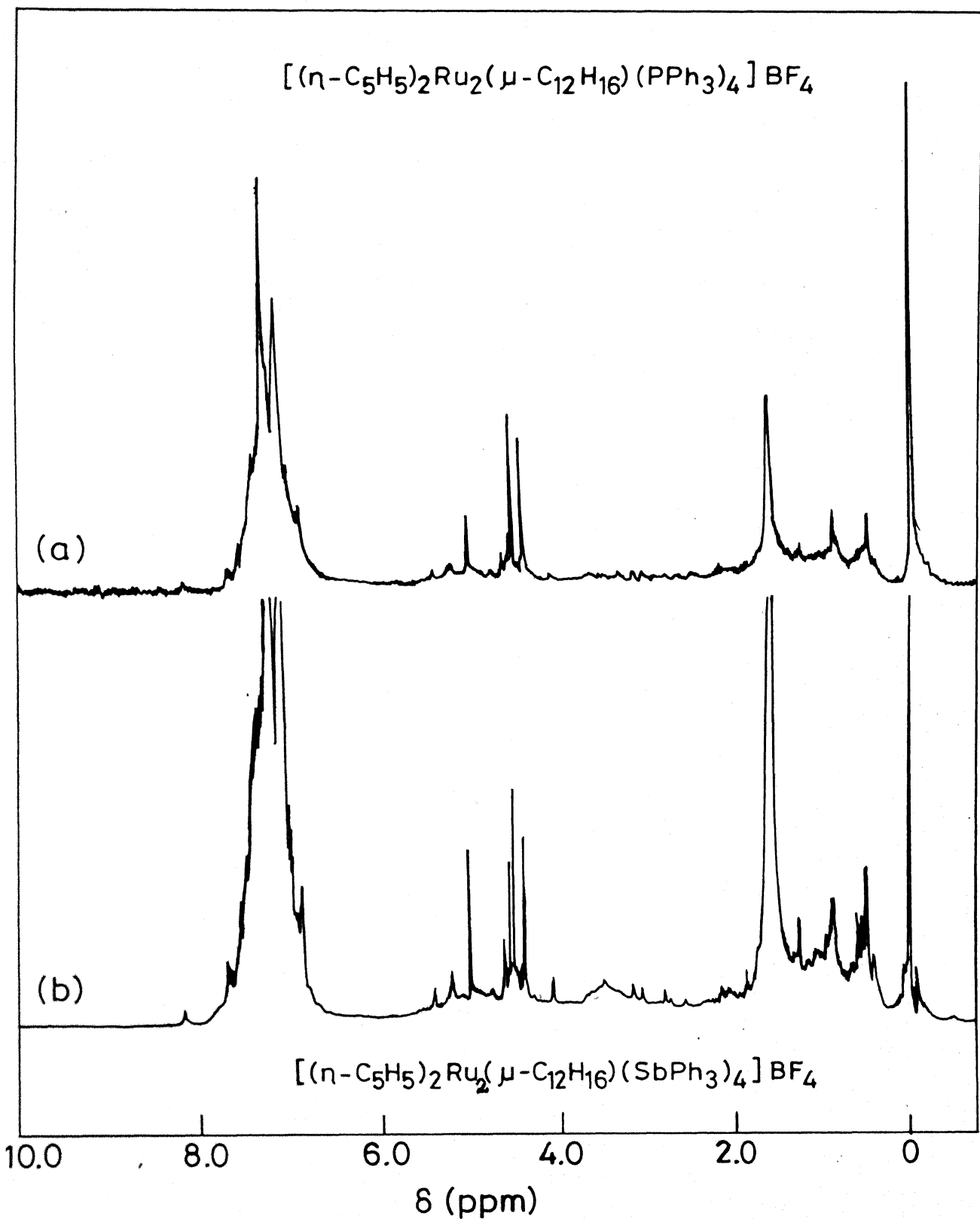


Fig.6.9  $^1\text{H}$  NMR spectra.

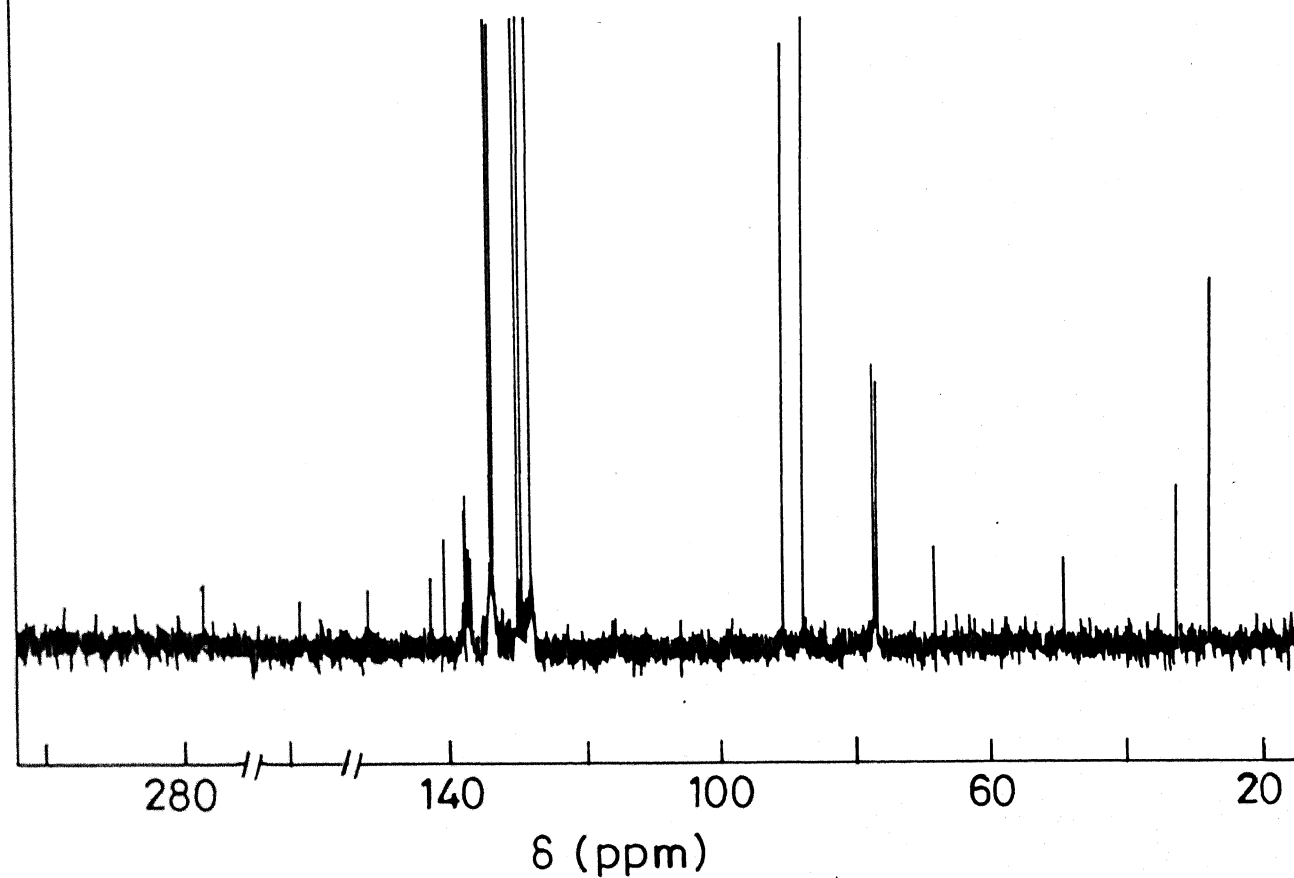
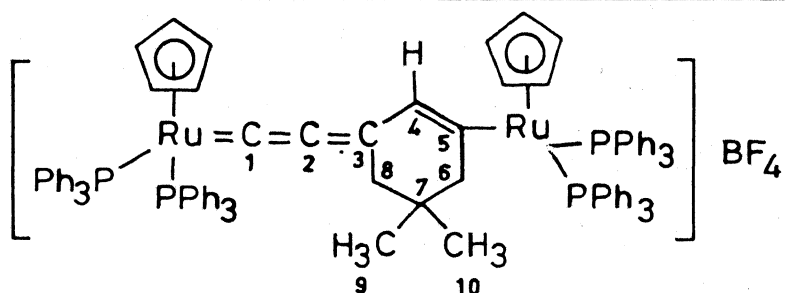


Fig. 6.10  $^{13}\text{C}$  NMR spectrum.

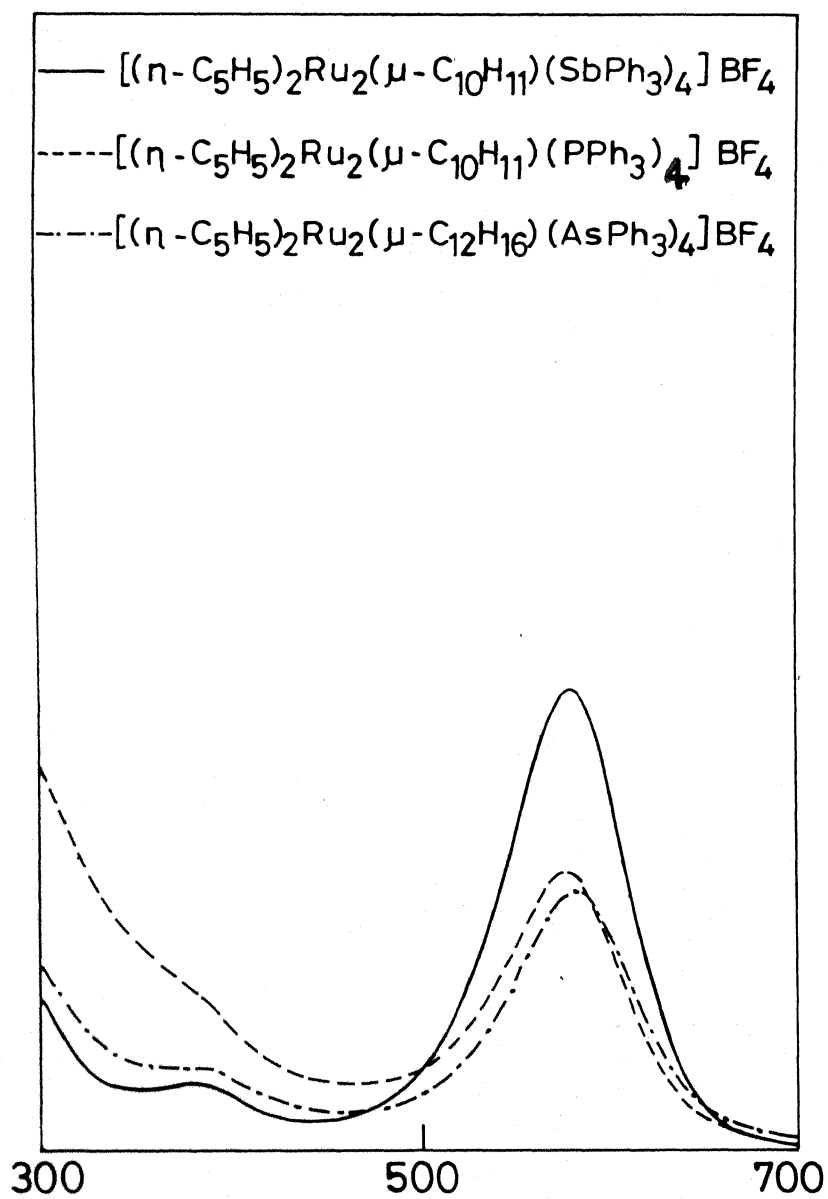


Fig. 6.11 UV visible spectra.

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## Chapter VII

### SUMMARY

A survey of literature in past two decades clearly indicates the synthetic versatility and the wide range of unusual chemistry displayed by the cyclopentadienylbis(triphenylphosphine)-ruthenium(II) complex,  $[(\eta-C_5H_5)Ru(PPh_3)_2Cl]$  and its analogues. The reasons for the unusual behaviour could be the result of: (i) high electron density on ruthenium and (ii) the steric interactions because of the presence of two bulky  $PPh_3$  groups (cone angle  $145^\circ$ ).

Although a large volume of work related to the synthetic and structural aspects of organometallic compounds has appeared in the literature, practically nothing is available regarding their triphenylarsine and stibine ligands analogue. The substitution of  $PPh_3$  ligand in the cyclopentadienyl-ruthenium(II) complex by triphenylarsine or stibine ligands could give rise to interesting properties of the compounds arising due to varied electronic and steric requirements of triphenylarsine and stibine from those of triphenylphosphine complex. In turn, the reactions of these

complexes with different N-bases like pyridine,  $\gamma$ -picoline, bipyridine, etc. could be studied. Since there exists a definite possibility to exhibit catalytic activity by these compounds, syntheses of cyclopentadienyl complexes of ruthenium with heterocyclic bases as coligands will significantly enhance the current efforts to widen the range of available potential of platinum group complex catalysts.

Followed by a concise overview of the reactions of  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{PPh}_3)_2\text{Cl}]$  first prepared by Wilkinson (1969) and latter by a facile one-pot, one step synthesis by Bruce et al. (1977), the first chapter of the thesis describes the scope and the objective of the work.

Chapters II and III describe: (i) the syntheses of complexes of the type  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{Cl}]$  ( $\text{E} = \text{P, As, Sb}$ ) and their interconversions, (ii) reactions of the product complexes,  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{EPh}_3)_2\text{Cl}]$  ( $\text{E} = \text{P, As, Sb}$ ) with halides and pseudo halides ( $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{NCS}^-$  and  $\text{H}^-$ ), (iii) insertion reactions of  $\text{SnCl}_2$  to form  $\text{SnCl}_3^-$  complexes and (iv) formation of cationic complexes of the type  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{L}]^+$  ( $\text{L} = \text{CH}_3\text{CN}$ ) with neutral ligands like  $\text{CH}_3\text{CN}$ .

The reaction details of N-bases like pyridine,  $\gamma$ -picoline 2,2'-bipyridine, orthophenanthroline and dithiocarbamate with  $\eta$ -cyclopentadienyl-ruthenium(II) complexes,  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$  ( $\text{E} = \text{P, As, Sb}$ ;  $\text{X} = \text{Cl, Br, I, CN, NCS, SnCl}_3$  and  $\text{H}$ ) were given

in Chapter IV. Reactions with bipyridine and o-phenanthroline yielded cationic complexes having the composition  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{EPh}_3)(\text{L-L})]^+\text{X}^-$  (where E = P, As, Sb; L-L = bipy or o-phen: X = Br, Cl, I, CN, NCS and  $\text{SnCl}_3$ ,  $\text{BF}_4^-$ ,  $\text{BPh}_4^-$  etc.) while pyridine and  $\gamma$ -picoline yielded neutral compounds of composition  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)\text{LX}]$  (E = P, As, Sb; L = Py or  $\gamma$ -pic; X = Cl, Br, I, CN, NCS,  $\text{SnCl}_3$ ). The reactions of the hydrido complex  $[(\eta\text{-C}_5\text{H}_5)\text{-Ru}(\text{EPh}_3)_2\text{H}]$  with 2,2'-bipyridine and o-phenanthroline formed cationic complexes in the presence of bulky counter anions ( $\text{BF}_4^-$ ,  $\text{BPh}_4^-$ ,  $\text{PF}_6^-$ ). Possible explanations for the different reactivity patterns are discussed in terms of chelation effect.

Formation of cyanobridged bimetallic complexes has been described in Chapter V. These were synthesized by reacting stoichiometric amounts of the cyano complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)\text{CN}]$  (1:1) with the halo complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{Cl}]$  in polar solvents in the presence of counter anions as  $\text{BF}_4^-$ . The cyanobridged compounds were characterised by various physicochemical methods (IR, proton NMR spectroscopy and microanalysis).

Reactions of complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{Cl}]$  with  $\gamma$ -hydroxy-acetylenes, phenylacetylene and their results have been reported in Chapter VI. In the case of phenylacetylene, vinylidene complexes having the composition  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2(\text{C}=\text{CHPh})]^+$  (E = P, As, Sb) were isolated. Propargyl alcohol yielded a mixture of the complexes having vinylidene as well as allenylidenes  $[(\eta\text{-C}_5\text{H}_5)(\text{EPh}_3)_2\text{Ru}=\text{C}=\text{CH}_2]^+$  as coligands. Allenylidene

derivatives were isolated exclusively with ethynylcyclohexanol. The reactions when carried out in the presence of  $\text{NaBH}_4$ , yielded neutral  $\eta'$ -alkynyl complexes of the type  $[(\eta\text{-C}_5\text{H}_5)(\text{EPh}_3)_2\text{Ru}(\text{C}\equiv\text{C-R})]$ .

Substituted propargyl alcohols  $[\text{HC}\equiv\text{CMeROH}]$  ( $\text{R} = \text{Me}$  or  $\text{Et}$ ) with the parent halide complexes formed the unexpected allenylidene-vinyl and vinylidene-vinyl complexes having the compositions  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}_2(\text{EPh}_3)_4(\mu\text{-C}_n\text{H}_m)]^{x+}$  ( $\text{E} = \text{P, As, Sb}$ ;  $n = 10$  or  $12$ ;  $m = 11$  or  $16$ ;  $x = 1$  or  $2$ ). The interconversions between allenylidene and vinylidene forms can be easily monitored by proton NMR and electronic spectroscopy.

In conclusion, the contents and the findings of the work embodied in the thesis are as follows:

- (1) The synthesis of  $\text{AsPh}_3$  and  $\text{SbPh}_3$  analogues of  $\text{PPh}_3$  complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  and the complexes of the type  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)(\text{E}'\text{Ph}_3)\text{X}]$  ( $\text{E} = \text{E}' = \text{P, As, Sb}$ ).
- (2) The interconversions of the complexes from one to another.
- (3) The reactivity of the complexes with halides ( $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ), pseudo halides ( $\text{NCS}^-$ ,  $\text{CN}^-$  etc.).
- (4) Insertion reactions with  $\text{SnCl}_2$  to form  $\text{SnCl}_3^-$  complexes.
- (5) The reactivities of  $\eta$ -cyclopentadienyl complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$  ( $\text{E} = \text{P, As, Sb}$ ;  $\text{X} = \text{Cl, Br, I, CN, NCS, SnCl}_3$  and  $\text{H}$ ) with N-donor heterocyclic bases (pyridine,  $\gamma$ -picoline, 2,2'-bipyridine, o-phenanthroline) and sulfur donor ligands, diethyl dithiocarbamate.

- (6) Isolation of cationic complexes of type  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)(\text{L-L})]^+\text{X}^-$  as a result of reactions  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$  with 2,2'-bipy or o-phen.
- (7) Formation of neutral monosubstituted complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)\text{LX}]$  (L = py or  $\gamma$ -pic) by reacting py or  $\gamma$ -pic with  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{X}]$ .
- (8) The formation of cationic complexes of the type  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)(\text{L-L})]^+\text{Y}^-$  by reacting hydrido complex  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{H}]$  with L-L = bipy or phen in alcoholic medium in the presence of bulky anion ( $\text{BF}_4^-$ ,  $\text{BPh}_4^-$ ,  $\text{PF}_6^-$ ).
- (9) Synthesis and characterisation of a variety of cyanobridged compounds.
- (10) Discussions on the lability of Ru-H bond in the complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{H}]$  in presence of halogen containing solvents like  $\text{CHX}_3$ .
- (11) Isolation of  $\eta'$ -vinyl and  $\eta'$ -allenylidene complexes by reactions of the parent halide complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{EPh}_3)_2\text{Cl}]$  with phenylacetylene, propargyl alcohol and ethynyl-cyclohexanol and the interconversion of vinylidene and allenylidene forms.
- (12) Formation of unexpected dinuclear cationic complexes by reacting halide complexes with substituted propargyl alcohol ( $\text{HC}\equiv\text{C-CR}_1\text{R}_2\text{OH}$ ).
- (13) Explanations for the formation of vinylidene, allenylidene and dinuclear cationic complexes. (A tentative mechanism is given.)

Despite the fact that there is a large and growing literature on the reactions of  $[(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{X}]$ , a great deal always remains to be discovered. A large number of interesting problems potentially solvable by the application of inorganic chemistry, may be posed. A few of these which are of some interest to us are the following.

(a) In view of the synthesis of triphenylphosphine analogue of the complex by refluxing  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  with  $\text{PPh}_3$  and  $\text{C}_5\text{H}_5$ , one should expect by substituting  $\text{PPh}_3$  with  $\text{AsPh}_3$  or  $\text{SbPh}_3$  to get its arsine or stibine analogues by the similar procedure. It is somewhat disconcerting to find that the same procedure is not applicable, why? Thus, a knowledge of factors important in the syntheses will be immense in the reply of this problem.

(b) The second problem even if the one cited in (a) is solved, is to know if the procedure is limited with phosphine only or can it be extended to the other ligands as well. If not, what are the reasons?

(c) All the syntheses so far carried out are by substitution of one or two of the ligands by other molecules. "Will it be possible to synthesize them starting from  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  or similar ruthenium salts"? A problem of much concern to us.

(d) The mechanism of the substitution reactions will be of a great consequence unravelling the mystery in the synthesis of the complex.

(e) We believe that in getting success in any reactions with the complex, degree of electron density on ruthenium plays an important role. A correlation, if one finds out, between the reactivity and the degree of electron density on the metal center will provide a clue for the future work.

(f) There is a possibility of using the nucleophilicity of N in the cyanide complexes in carrying out a large number of Ritter-type of reactions, which will prove to be invaluable in the organic synthesis or in the synthesis of novel inorganic complexes. Analogues to this, the electrophilicity of the  $\alpha$ -carbon and nucleophilicity of  $\beta$ -carbon may also prove to be very helpful in synthetic reactions.

(g)  $CYX$  ( $X, Y = O, S, Se$ ) insertion between  $Ru-H$ ,  $Ru-Cl$ ,  $Ru-CH_3$  bond in the complexes  $[(\eta-C_5H_5)Ru(EPh_3)(L)X]$  [ $E = P, As, Sb$ ;  $L =$  any monodentate ligand;  $X = H, CH_3, Cl$ ] will be a interesting study.

(h) These insertion reactions can be further extended to other small molecules.

(i) The reactions of  $NOX$  with vinylidenes, allenylidenes, acetylenes and bridged vinylidenes will make an exciting study.

The problems, cited in the preceeding paragraphs, are only a few among the infinite ones and the convergence of physical and analytical techniques combined with inorganic and organic theories



make this study the most exciting ones. We have to combine the hard facts and the principles of inorganic discipline to understand the fascinating mysteries of this molecule.

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# LIST OF PUBLICATIONS

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